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On the chemical evolution and densities of the planets*

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Abstract—It is assumed that planets have accreted at low temperature from a cloud of dust and gas of cosmic composition. Subsequent melting may cause reduction of metallic oxides by carbonaceous compounds which were trapped during accretion. The metal so produced would segregate and form a core. Chemical evidence indicates that the metallic phase would consist chiefly of iron, nickel and silicon. The higher the reduction temperature, the higher will be the content of silicon in the nickel–iron. The density variation of terrestrial planets can be explained by differing degrees of reduction of the primitive non-volatile material. According to this view, Mars is composed of completely oxidized cosmic non-volatile material, whereas Mercury is highly reduced, with most of its silicon occurring in the metal phase. Venus, the earth and meteorites exhibit intermediate stages of reduction, and therefore, intermediate densities.

Examination of the chemistry and mineralogy of meteorites supports the suggested theory of origin. The mineralogy is similar to blast-furnace assemblages, suggesting analogy between the processes of metal production. Prior's rules, concerning the inverse variation of oxidized and reduced iron in meteorites, and nickel content of chondritic iron, are readily explained. The reduction hypothesis provides a mechanism for chondrule formation. Textural and chemical evidence indicates that they formed within the meteoritic planet by rapid crystallization due to loss of water below 1000°C.

If meteorites and the earth are to possess similar non-volatile compositions, the earth's core must contain about 20 per cent of silicon. Occurrence of some silicon in the core would enable explanation of its probable density and elasticity, which are not satisfactorily explained by the properties of pure nickel–iron.

When the metal which is produced by reduction near the surface of the earth segregates to form a core it is out of chemical equilibrium with the mantle because the high temperatures and pressures at the core–mantle boundary displace the equilibria. The reactions chiefly concerned are:

$$Ni^{\circ} + Fe^{++} = Ni^{++} + Fe^{\circ}$$

$$Si^{\circ} + 2Fe^{++} = Si^{++++} + 2Fe^{\circ}$$

A substantial e.m.f. is therefore generated at the core–mantle boundary. This may be of importance in connexion with the theory of the earth's magnetic field. Accompanying ionic diffusion effects near the boundary may cause density changes and convection in the core. Resultant changes in the composition of the mantle near the boundary may be responsible for the change in gradient of seismic velocities observed by Jeffreys and Gutenberg. A further effect of this process is to cause a steady contraction in the volume of the core.

1. Introduction

Most theories of the origin of the solar system may be classified according to whether they advocate a hot or cold origin for the primitive material. Urey (1953 and other references) has discussed the chemical evidence and advanced several arguments suggesting that the earth, moon and meteorites were initially formed at low temperatures. Perhaps the most important of these are:

(1) The oxidized iron in the earth and meteorites could not have existed in the presence of gases of cosmic composition at a temperature of more than a few hundred degrees (centigrade). Reduction to metal would occur if the temperature was any higher. A similar argument applies to iron sulphide in meteorites.

(2) It is difficult to understand how any water, nitrogen, carbon and other

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volatile elements were retained in the earth if it condensed from gases of cosmic composition at high temperatures.

Urey (1952) has pointed out that these data seem most compatible with a hypothesis suggested by Von Weizsacker (1944) and further developed by Kuiper (1955). The basic postulate is that planets have condensed from a cold cloud of gases and dust of cosmic composition. This general model is assumed in the present discussion.

Since the dust cloud was presumably chemically homogeneous, the observed variation of density in the inner* planets (Table 1) necessitates some sort of

Table 1. Mean densities of planets (g/cm^3) (Kuiper, 1952)

Mercury	5·46	
Venus	5·06	
Earth	5·52	Inner planets
(Moon)	3·33	
Mars	4·12	
Jupiter	1·35	
Saturn	0·71	
Uranus	1·56	Outer planets
Neptune	2·47	
Pluto	2?	

chemical differentiation of the primitive material. As Latimer (1950) and Urey (1952) have shown, the primitive non-volatile material would be oxidized in the presence of gases of cosmic composition at low temperature. This conclusion is particularly important in the case of iron.

Partial reduction of the oxidized dust has subsequently occurred in the earth and in meteorites, and must be assumed for other planets if their densities are to be explained. In the earth, and in meteorites, the principal elements formed by reduction have been iron and nickel.

Urey (refs.) has extensively discussed the reduction process required. Most of his suggested models employ hydrogen as the reducing agent. Reduction by hydrocarbon free radicals has also been recently suggested (Urey, 1956). Urey concluded that reduction alone is insufficient to account for the density variation of terrestrial planets and assumed that selective removal of silicate material from metal was also required. Difficulties were encountered in suggesting a satisfactory mechanism for this fractionation, and in the opinion of the author, no convincing solution has been offered.

In the present paper an attempt is made to show that planet densities are explicable in terms of oxidation–reduction equilibria affecting the primitive cosmic dust, and that the assumption of silicate–metal fractionation is unnecessary. *It is suggested that the ratios of non-volatile elements† are the same on all planets,*

* The low densities of the outer planets are satisfactorily explained by the presence of large quantities of condensed gases which were unable to escape by evaporation due to low temperatures and large masses of these planets.

† These may be defined arbitrarily according to whether or not they are volatile at 500°C in the presence of gases of cosmic composition (Table 2).

but that the state of oxidation (i.e. the ratio of oxygen to metal) may vary in different planets. The smaller the oxygen content of a planet, the higher will be its density.

Before describing a mechanism which might account for the differing stages of oxidation in planets, it is well to consider evidence relating to the suggestions above.

Perhaps the strongest evidence in favour of constant ratios of non-volatile elements in all planets is negative—the difficulty of inventing a satisfactory mechanism for fractionating the non-volatile elements. Further evidence has recently become available. Birch (1958) has pointed out that the total heat flow observed at the surface of the earth divided by the mass of the earth closely approximates the generation of radiogenic heat in chondritic meteorites. This suggests that the mean contents of U, Th and K are the same in meteorites and the earth. Since these elements are characteristically strongly fractionated by crystallization and/or volatilization processes, it would appear that little relative differentiation in composition has occurred between earth and chondrites. A further indication of the chemical resemblance between the silicate phase of stony meteorites and the earth's mantle is that elemental abundances in the former provide a satisfactory model for inferring and explaining the properties of the latter (Ringwood, 1958b).

If the metal phase in planets has been derived by a process of reduction of primitive oxidized material there does not seem any apparent reason why the reduction should proceed to the same extent in all planets. Differences in the final oxidation state would be anticipated. In fact such differences are demonstrable. The average MgO/FeO ratio in chondritic meteorites is 2, whilst in the earth's mantle it is close to 5 (Section 5).

2. The Reduction Process

(a) *General outline*

The model adopted assumes that planets accreted at low temperatures ($\sim$0°C) from a cloud of dust and gas originally of cosmic composition (Table 2). It is suggested that carbonaceous compounds collected together with the oxidized dust and were buried in the accreting planet. Rising temperature in the planet caused melting and convection. The trapped carbon reacted with the oxidized melt causing reduction, and separation of a metallic phase consisting dominantly of iron, nickel and silicon. The gaseous reduction products—carbon monoxide and carbon dioxide—rose through the melt to the surface of the planet where they escaped by evaporation. Further aspects of this model must be considered in detail.

(b) *Burial of carbonaceous material*

Significant amounts of graphite and carbonaceous material occur in many iron and stony meteorites. Accordingly conditions during formation of meteorites must have favoured the existence of condensed carbonaceous compounds. If chemical equilibrium occurred in the dust cloud, carbon would occur in the form of methane, which would condense around dust grains because of the probable low temperature in the cloud (perhaps $\sim$30°K; Dufay, 1957). At this early stage of cosmic evolution

the dust grains may have been highly radioactive, due to unstable short-lived nuclides and increased activity of the U, Th, K series. Intense radioactive bombardment of the methane rims would cause decomposition and loss of hydrogen, accompanied by polymerization and formation of carbonaceous compounds of lower volatility. These compounds would accompany the dust during accretion into a planet, even if accretion occurred at significantly higher temperatures, e.g. around 300°K.

Table 2. Cosmic abundances of the elements (Kuiper, 1952)

Element	(Log abundance)
H	10·10
He	9·24
O	6·70
Ne	6·77
N	6·48
C	6·14
A	5·9
Mg	5·59
Si	5·56
Fe	5·29
S	5·19
Cl	5·10
F	4·60
Al	4·50
Ca	4·40
Na	4·25
Ni	4·14
P	3·80
Mn	3·46
Cr	3·52
K	3·38
Co	3·02
Zn	3·00
Ti	2·98

Unstable carbonaceous compounds of low volatility may also condense directly from the gas phase in the dust cloud. (Urey and Donn, 1956). See also Section 2c (ii). Under the extremely low temperatures and pressures involved, attainment of chemical equilibrium would be unlikely.

(c) *The melting process*

The factors controlling melting in the accreted planets are likely to have been complex. At least four large sources of energy were probably involved, but it is not yet possible to quantitatively evaluate their rôles. The relative importances of these sources may have varied in different planets.

(i) *Radioactive heating.* The importance of this source of heat depends on the times which have elapsed between nucleogenesis, condensation of dust from gas,

accretion of dust into planets and melting in the planets. If the time between nucleogenesis and accretion was of the order of 10^6–10^7 years, radioactive elements with short half lives may well have contributed enough energy to cause melting and reduction (UREY, 1955). There is also a possibility that nuclides presently unknown may have contributed substantially to the heating (KOHMAN and SAITO, 1954). On the other hand, if the interval between accretion of dust into a planet and melting within the planet was sufficiently long an important contribution to heating would be made by the U, Th and K series.

"Fossil radiogenic energy" may also have been significant. Carbonaceous compounds produced by low-temperature radiogenic decomposition of condensed methane in the dust cloud may be unstable. Such compounds, e.g. acetylene, would be trapped in the accreting planet and would decompose exothermically as temperature rose. A further energy contribution comes from stored radiation damage* to the silicate nuclei of the grains. This could be substantial at very low temperature and would be released as the interior of the planet warmed up.

(ii) *Chemical heating.* The importance of this energy source was first appreciated by UREY and DONN (1956). It seems probable that the dust grains condensed from interstellar gas at extremely low pressure and temperature (DUFAY, 1957). Under such conditions attainment of chemical equilibrium would be most unlikely. The nature of the particles would be controlled by kinetic considerations and highly unstable configurations would result. UREY and DONN pointed out that condensed free radicals and unstable molecules would probably occur in the dust. Groups such as CH, CH^+ and CN are common in cold interstellar gas. Dust grains would not consist of recognisable silicate minerals, but of random aggregates of atoms of low volatility together with free radicals and unstable molecular groups composed of C,H,N and O atoms and ions.

Such dust grains, if incorporated into an accreting planet at sufficiently low temperatures, could supply ample energy by exothermic decomposition to support heating, melting and reduction. UREY and DONN pointed out that energies evolved by decomposition of the free radicals most likely to be involved amount to several thousand calories per gram.

The amount of chemical energy which is available to cause heating in a planet decreases as the temperature of accretion increases, due to decomposition of free radicals and unstable molecules before burial. An accretion temperature less than 100°K would probably be necessary to allow burial of condensed free radicals in a planet. However other molecular groups such as acetylene would be more stable and could be trapped and buried at accretion temperatures up to 200°K.

(iii) *Gravitational energy due to core formation.* After one of the foregoing energy sources had caused melting and reduction in a planet, the sinking of metal in the gravitational field of the planet causes a substantial evolution of thermal energy. UREY (1952) estimated that the energy associated with core formation in the earth was about 700 cal/g for the whole earth. This could cause widespread melting and reduction with considerable rapidity.

(iv) *Gravitational energy of dispersed dust.* A cloud of dispersed dust possesses

* This suggestion was made to the author by Professor FRANCIS BIRCH.

considerable potential energy due to the mutual gravitational attraction of the particles. Latimer (1950) estimated that accretion of the earth from dust would require dissipation of 10,000 cal/g for the whole earth. For any planet, the amount of gravitational energy varies approximately as the square of the radius. This energy must be dissipated as heat and radiation when the dust collects into a massive body. Some of this energy would also be used in evaporating volatile components from dust grains.

The prime importance of this energy source is in determining the temperature of accretion. This in turn determines how much available energy of chemical or fossil radiogenic origin will be incorporated within the planet. This decreases with increasing accretion temperature (Section 2cii).

(d) *Some chemical principles involved in the reduction process*

The reduction of oxidized metallic compounds is of fundamental importance in extractive metallurgy and a large body of information on the relevant reactions is available. The free energies of formation of some common oxides at 1500°C are listed in Table 3 (data from Richardson and Jeffes, 1948). The sequence in Table 3 indicates the "ease of reduction" of metallic oxides.

Table 3. Free energies of formation of some metallic oxides at 1500°C

Oxide	$-\Delta G$ (kcal)
$2NiO$	33
$2CoO$	52
$2FeO$	73
$\frac{4}{3}Cr_2O_3$	105
$2MnO$	121
SiO_2	131
TiO_2	144
$\frac{4}{3}Al_2O_3$	179
$2MgO$	179
$2CaO$	215

The common oxides most easily reduced are those of nickel and iron. It is important to note that the next common oxide in the series is silica. In minerals, these oxides occur combined as silicates. However, the free energies of formation of silicates from oxides are small compared with the free energy of formation of the individual oxides, and the equilibria involving the oxides may therefore be considered as a good approximation.

According to the mechanism suggested in 2(a), reduction of primitive oxidized non-volatile material is effected by carbonaceous compounds. In principle, the most important reactions involved reduce to:

$$FeO + C = Fe + CO$$
$$FeO + CO = Fe + CO_2$$
$$SiO_2 + 2C = Si + 2CO$$

Reactions analogous to those for iron apply in the case of nickel and cobalt. In addition, some reduction of ferro–metal oxides is probably carried out by hydrogen which was trapped in the planet in the form of condensed hydrocarbons:

$$FeO + H_2 = Fe + H_2O$$

For these reactions to proceed in a planet, melting is necessary. This may be caused by one of the methods discussed in the previous section. As long as the primitive mixture of oxidized material and carbonaceous compounds is confined in the solid interior of the planet, no reduction is possible because the gaseous reaction products (CO, CO_2, H_2O) are unable to escape. When melting and convection occur, the carbonaceous compounds trapped in the interior rise towards the surface in contact with oxidized metallic compounds. When the liquid reaches the surface regions, the confining pressure drops sufficiently to allow escape of

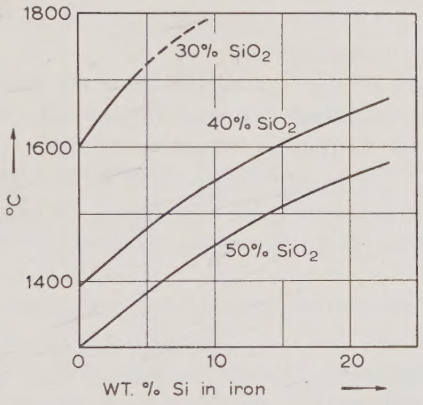

Fig. 1. Silicon content of iron in equilibrium with $CaO–SiO_2$ melts containing 10 per cent Al_2O_3, as a function of temperature and composition. The system is saturated with carbon and in equilibrium with one atmosphere of carbon monoxide (data from FULTON and CHIPMAN, 1954).

CO, CO_2 and H_2O as gas bubbles. Rapid reduction and gas evolution ensue, metallic iron is produced, and the mixed magma and iron sinks to be replaced by a fresh surge from below. The metal so produced could eventually segregate and form a core.

The minimum temperature at which liquid would form from a melt of oxidized primitive (chondritic) composition (Table 4, column 6) is around 1100°C at zero pressure. Higher pressures in the interior of the planet would increase this value, but the increase would probably be offset by the presence of water, which would lower the melting temperature.

The extent to which reduction proceeds depends upon several factors, most important of which is the temperature. As this increases, more and more iron becomes reduced, and then silica becomes reduced to silicon. Since this is miscible with liquid iron, this effect manifests itself by an increasing content of silicon in the metallic phase which separates.

Figure 1 illustrates the effect of temperature and composition upon the silicon content of iron in equilibrium with a carbon saturated melt at one atmosphere of carbon monoxide (data from FULTON and CHIPMAN, 1954). The melts are composed

of CaO and SiO_2 in varying proportions, and contain 10 per cent of Al_2O_3. This differs from the natural case in which MgO would be substituted for CaO. However Fulton and Chipman showed that substitution of MgO for CaO has little effect on the equilibria. On a mole per cent basis this tends to increase slightly the content of silicon in the metal phase. Accordingly the data in Fig. 1 are of considerable significance. It may be observed that:

(1) The silicon content of the metal increases rapidly with temperature above 1300°C.

(2) The silicon content of the metal decreases with decreasing content of SiO_2 in the melt.

Reduction removes iron oxide from the silicate liquid thus increasing its melting temperature, and causing crystallization of magnesian silicates. The energy required is partly supplied by the latent heat of crystallization. Reduction therefore occurs at a relatively constant temperature, and ceases when the residual liquid has been completely crystallized.

If the initial temperature of the liquid is sufficiently high (~1500°C according to Fig. 1) reduction of SiO_2 to silicon becomes important. This also increases the melting temperature, and for complete reduction of SiO_2, a temperature around 2000°C would be necessary. The temperature of reduction therefore governs both the equilibrium amounts of iron and silicon in metal and silicate phases, and the actual mechanism of reaction—since liquid is required for the continuance of the process.

It is probable that kinetic factors would be of considerable importance in the reduction process, as in blast furnace operations. In an extremely complex operation such as that contemplated, involving huge volumes of reacting materials, it is hardly likely that overall equilibrium would be reached. Reduction of rising magma would be rapid, and considerable local compositional inhomogeneity would be expected. The net effect observed would depend on how thorough the subsequent mixing by convection was. This must be remembered when laboratory chemical equilibrium data are applied to the natural process. The retention of small quantities of water, nitrogen and carbon in solution in the melt may be attributed in part to non-attainment of equilibrium.

The transfer of iron and silicon from the oxidized to the metallic phase results in an increase in density of the planet. The density of completely oxidized chondritic material (Table 4, column 6) is 3·57 g/cm³. Complete reduction of iron and nickel increases the density to about 3·9. With more intense reduction the iron carries down some silicon in solution. Transfer of silicon from silicate to metallic phase causes a rapid increase in density (Fig. 2) which may rise to 4·85 g/cm³ for the case of complete reduction of SiO_2. In such a fashion the density variation among planets may be interpreted.

(e) *Energy requirements for reduction*

The reduction process previously suggested is endothermic. The most important equations for estimating energy requirements are as follows.

$$FeO + C = Fe + CO \qquad \Delta H = 29{\cdot}5 \text{ kcal (1500°C)}$$

$$SiO_2 + 2C = Si + 2CO \qquad \Delta H = 150 \text{ kcal (1500°C)}$$

Calculations show that the energy required for reduction in the Earth and in Venus is about 350 cal/g of the primitive oxidized body. This is probably about one-third of the energy per gram needed to cause complete melting throughout the whole body. In the case of the meteoritic planet the energy required to produce the observed amount of metal by carbon reduction is approximately 90 cal/g—about one-fifth of the energy required for complete melting, and somewhat less than the latent heat of melting.

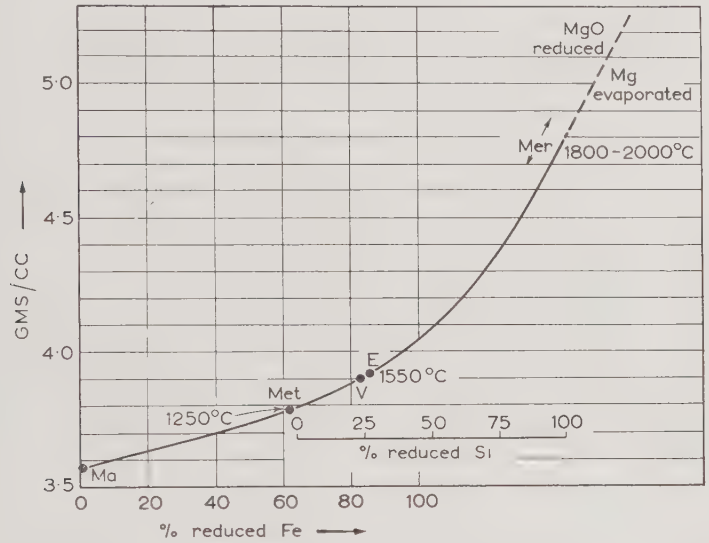

Fig. 2. Showing the increase in density of primitive oxidized non-volatile material as iron oxide and silica are reduced to metal. Estimated temperatures or the corresponding stage of reduction are indicated. The letters *Ma*, *Met*, *V*, *E*, and *Mer* refer to the probable positions of the inner planets on this curve. (In calculating the densities of the silicate phase, sodium and aluminium have been calculated as jadeite rather than albite. This procedure was adopted in view of experiments (Robertson *et al.*, 1957) which show that felspar will break down to denser phases at shallow depths in planets where they occur. The density of silicon–iron alloys was taken from Greiner *et al.*, 1933.)

These requirements are not excessive and could be supplied by the energy sources suggested in Section 2(c) without making improbable assumptions. It is possible that the energy was supplied by a combination of the different sources.

The high degree of reduction apparently occurring in Mercury requires a large energy supply—about 1200 cal/g of the original oxidized material. This is about twice the total heat required for melting from an initially cold state. Furthermore this energy must have been supplied in a short time. It seems that it must be derived from chemical and fossil radiogenic sources. (Section 2(c)). This would require that Mercury accreted at a very low temperature thus permitting trapping and burial of highly unstable dust.

(f) *Escape of reduction products*

The reduction process would cause evolution of enormous volumes of CO_2, CO and H_2O at the surface of the planet. In the case of the earth, the earliest rocks show no signs of being subjected to an atmosphere of this type (Rubey, 1955).

A critical requirement of the hypotheses therefore is that the gaseous reduction products escaped from the earth by evaporation during and immediately after the reduction process. This may require a combination of high surface temperatures, rapid rotation and, perhaps, high energy corpuscular bombardment and radiation from the sun or stars.*

The atmospheric temperature in the final stages of the accretion process would be very high. Dust with an energy of 10,000 cal/g would be falling into a dense atmosphere of CO_2, CO and H_2O which had been derived from the reduction process. The dust would "burn up" as in meteors and rapidly transfer its energy to the atmosphere. In this manner, high temperatures might be attained, enabling the gases to escape by evaporation.

As Rubey (1955) has pointed out, the present atmosphere probably developed subsequently by "degassing" of the outer parts of the earth.

3. Some Aspects of the Chemistry of Meteorites and their Bearing upon the Reduction Hypothesis

The proposition that meteorites represent fragments of a disrupted former planet appears very plausible. Recent studies of crystallization pressures indicate that the meteoritic planet was at least as large as the moon (Lovering, 1957). However, the methods used in calculating the internal pressures tend to give minimum values and the possibility remains that the planet was substantially larger than the moon.

Of the many varieties of meteorites, chondrites and siderites are by far the most abundant. The former presumably represent the mantle of the former planet, whilst the latter represent the core. Transitional between these are the pallasites, consisting of mixed metal and olivine. Chondrites usually contain variable amounts of metal which apparently was unable to settle out into the core.

The compositions of chondrites furnish valuable evidence on the role of differential reduction in their genesis. The analysis quoted in Table 4 is an average value for chondrites.† There is a wide variation in the relative amounts of nickel–iron, oxidized iron and nickel content of irons. An investigation of this variation by Prior (1916) established two important rules.

(1) An inverse relationship exists between the amounts of metallic and oxidized iron in chondrites. The total amount of iron is approximately constant.

(2) The nickel content of the iron in a chondrite increases as the total amount of iron phase decreases.

Prior furthermore noted that the total overall composition of chondrites was relatively uniform if the state of oxidation of iron was neglected. He suggested

* Magnetohydrodynamic effects may also have been important. After the core had segregated, cooling may have been very rapid initially because of high radiant heat conductivity in the mantle (Lawson and Jamieson 1958). This would cause strong convection currents in the core leading to more powerful magnetic fields at the surface of the Earth than are known today. Such fields, interacting with a hot ($>1500°C$), turbulent, ionized atmosphere of CO_2, CO and H_2O may have been an important factor controlling evaporation and escape.

† Urey and Craig (1953) and Wiik (1956) have studied the compositions of chondrites. They conclude that they fall into two groups, characterized by distinct metal-silicate ratios. Urey and Craig suggest that the grouping could be caused by two separate parent meteorite bodies. An alternative view would be that some sinking and segregation of iron had occurred in part of one parental meteoritic planet.

that the above rules were to be explained in terms of a variable state of oxidation of primitive material. Brown and Patterson (1948) have also pointed out that oxygen is the principal variable in chondrites. Prior tried to account for the variation in the opposite sense to that suggested herein. He assumed that meteorites represent varying stages of oxidation of a primitive metallic body consisting of an alloy of the common metals in the proportions occurring in meteorites. This suggestion is no longer attractive, but the rules discovered by Prior, and his realization that their explanation lay in the concept of variable oxidation remain of the utmost importance. The view suggested in this paper is, in general agreement with Prior but maintains with Urey and Latimer, that the original state of cosmic material was oxidized, not reduced.

Prior's second rule is simply explained on this model. Nickel is the easiest of the common metals to reduce from its oxide, and therefore the first metal to be formed is rich in nickel. As more and more iron is reduced, the nickel content falls, giving rise to an inverse relationship between nickel content and total amount of metallic iron.

The substantial amount of nickel–iron trapped in the silicates suggests that complete melting was never attained. Reduction apparently commenced as soon as a relatively small amount of melting allowed carbon monoxide to escape, most of the reduced metal being retained in the crystal mesh.

The widely varying degrees of oxidation observed in chondrites demand considerable variation of temperature and pressure conditions during reduction, and also require that no remixing has taken place after reduction. Discussion in the previous sections suggest that these conditions are likely to be supplied by the suggested mechanism.

The mineralogy of meteorites is strongly suggestive of a blast furnace operation. A ubiquitous accessory mineral in siderites is schreibersite, $(FeNi)_3P$. The corresponding compound Fe_3P is also found widely in blast furnace irons. Phosphates are easily reduced by carbon at high temperatures and the phosphorus readily alloys with iron. Carbon, as graphite and cohenite, $(FeNi)_3C$, is common in siderites as well as blast furnace iron. In the latter case the corresponding carbide is cementite, Fe_3C. Moissanite (SiC) is known in meteorites, and has also been formed in iron saturated with carbon and silicon during experimental investigations relating to blast furnace operation (Fulton and Chipman, 1954). It is worth noting that the common gases found in iron meteorites are CO, CO_2, H_2 and CH_4 (Farrington, 1901). The first three are also found in blast furnace iron. The common occurrence of this group of minerals and gases in both environments suggests that the chemical processes which produced meteoritic iron and blast furnace iron have been similar, i.e. that the iron in meteorites has been produced by reduction in the presence of carbon.

The behaviour of sulphur provides further support for this view (Hopkins, 1957; Hatch and Chipman, 1949). In metallurgical operations sulphur is usually partitioned between slag and metal. For material of meteoritic composition, most sulphur would probably occur in the silicate phase. This relationship is observed in meteorites where most of the sulphur is found in chondrites, not irons. The sulphur in chondrites was apparently originally in solution in the silicate phase, and has

crystallized as troilite on cooling. When strong reduction of a slag occurs, concurrently with high temperatures, metallurgical experience is that sulphur is strongly concentrated in the slag, from which it crystallizes as calcium sulphide. This mineral occurs in some meteorites as oldhamite under completely analogous conditions. Stony meteorites containing oldhamite are found to contain very little oxidized iron and have therefore been strongly reduced at high temperature. Complete or partial obliteration of former possible chondritic structures due to recrystallization accompanying high temperature is also characteristic of oldhamite containing meteorites.

Textures of Stony Meteorites

Interpretation of stony meteorite textures has strongly influenced ideas on their genesis. It is necessary that the suggested model of meteorite evolution should be able to account for them. The great majority of stones possess the characteristic chondritic texture—small spheres and spheroids of olivine, pyroxene and sometimes "glass" (chondrules) scattered throughout a finely and irregularly crystallized matrix of the same minerals, together with nickel–iron and troilite. Crystallization patterns within chondrules are extremely varied and often complex. Chondrites are sometimes highly friable.

It is usually maintained that chondrites are tuffaceous and fragmental in origin, and that the chondrules are former free drops of molten silicates which have been chilled. It has proved difficult to reconcile this view with the evidence that meteorites, of which chondrites are by far the most common variety, were once part of a large cosmic body which had melted and differentiated. A possible explanation is suggested below. It follows naturally from the model of planet evolution discussed in previous sections. It maintains that chondritic textures originated during the primary crystallization processes which occurred in the meteoritic planet and that chondrules were *not* formed from free, molten, silicate drops.

The primitive oxidized dust which accreted to form the meteoritic planet would contain considerable quantities of ice or water, which would become trapped internally. When melting occurred in the interior of the planet, the liquid would be saturated with water, resulting in a considerable lowering of the melting temperature. According to the model, the water-saturated magma then rises to the surface of the planet where reduction of iron oxides by carbonaceous material takes place. Simultaneously the dissolved water is rapidly liberated. Since the liquid is considerably below its dry melting point it undergoes rapid crystallization simultaneously with reduction.

Under such conditions, chondrules could be formed in three ways.

(a) *By spherulitic crystallization*

Spherulite formation is a very common mode of crystallization in a wide variety of rapidly cooled and supersaturated liquids, including silicate melts. In the case under discussion, rapid supersaturation is achieved by loss of water from the melt. Under these conditions, spherulitic crystallization might be expected. In spherulites, crystallization starts at a nucleus and proceeds outwards. The shape

of the aggregate depends principally upon diffusion of ions to and from the nucleus. This gives rise to a spheroidal form. Outward conduction of latent heat may also be important. Crystallization within the spheroid need not possess radial symmetry, although it often does. This is controlled by the habit and properties of the crystal nucleus and a wide variety of growth patterns is to be expected. Patterns in which the growth is parallel to the faces of the nucleus would be common.

Chondrules for which a spherulitic origin is suggested include those with hour-glass structures, and those consisting essentially of pure pyroxene and olivine. These latter may occur as large single crystals (monosomatic), aggregates of single crystals (polysomatic) or possess the radiating fibrous structure characteristic of many chondrules. This is also very common in spherules.

Spheroidal shapes of single crystals and groups of crystals are formed under conditions of rapid crystallization (Buckley, 1951). This is a consequence of equality of crystallization velocities in all directions, which prevents development of crystal faces.

(b) *By reduction*

Reduction of oxidized magma near the surface depletes the liquid in iron. Any pre-existing ferromagnesian minerals are therefore thrown out of equilibrium with the liquid. To regain equilibrium they must recrystallize and simultaneously precipitate metallic iron. This could be responsible for the occurrence of chondrules with rims of metallic iron, which are occasionally found.

(c) *By cavitation*

Sudden evolution of steam from the melt will cause intense cavitation, fragmentation and formation of new surfaces. Melts of chondritic composition possess low viscosities and high surface tensions. It seems possible that as a transitory stage during simultaneous crystallization, reduction and loss of water, the cavitation would allow surface tension forces to operate, producing spheroidal "drops". These "drops" would possess only a very short lifetime since they would instantly crystallize. They are not comparable with the "dispersed molten drops" from which chondrules are believed to form according to most current theories.

It is suggested that such a process could be responsible for chondrules containing idiomorphic phenocrysts of olivine and pyroxene in "glass", and also for chondrules which are well crystallized around the margins, but which contain inclusions of glassy material toward the centre.

Some detailed features of chondrites are now considered—with particular reference to the hypothesis previously presented, and the classic hypothesis, which regards the chondrules as former dispersed molten drops of silicate material. In subsequent discussion, the latter will be called the "free drop" hypothesis.

(i) *Crystallization pattern of chondrules.* Many of the fibrous radiating textures found in chondrules could be equally caused by spherulitic crystallization in a homogeneous medium or by crystallization of discrete molten drops. However the perfect hour-glass structures occasionally displayed by chondrules are almost certainly due to spherulitic growth from a central nucleus. It is most unlikely that these would form from cooling liquid drops.

Numerous chondrules are found (Farrington. 1901) with rims of metallic iron or sulphides. Finely dispersed troilite crystals are frequently concentrated in the outer parts of chondrules. This suggests that these chondrules have grown outwards as in spherulites, pushing troilite and iron towards the margin. In a chilled drop, crystallization occurs from the margins inwards. Thus, metal and sulphides should be concentrated in the centre.

(ii) *Composition.* Chondrules are almost exclusively composed of olivine, pyroxene and glass in varying proportions. In many cases they consist of pure olivine and/or pyroxene. The free-drop hypothesis cannot explain the mineralogical purity of these chondrules. This is easily explained however if they originated by rapid crystallization within the melt, the spheroidal forms being caused by high crystallization velocities, as previously suggested.

(iii) *Cooling mechanism.* Textures of chondrules show that they have crystallized very rapidly. Detailed examination of chondrites shows that this is also true of the crystals forming the matrix. Inclusions and intergrowths of glass and other minerals, indicative of rapid crystallization are characteristic of groundmass as well as chondrules.

Now melts which consist dominantly of olivine and pyroxene crystallize extremely rapidly into well-formed crystals. They cannot be supercooled unless quenching occurs in a matter of seconds. The fibrous textures and the poorly crystallized intergrowths of glass, olivine and pyroxene so common in chondrites indicate that crystallization has occurred in a matter of minutes, or even seconds. Since chondrites are by far the most abundant stony meteorites this means that most of the silicate portion of the meteoritic planet has crystallized in times of this order.

Such rapid crystallization cannot be explained by any *cooling* process known to the author. This would require a prodigous dissipation of heat in a very small time. The assumption that cooling followed a collision in which the meteoritic planet was thoroughly disintegrated does not solve the problem.

The present hypothesis assumes that rapid crystallization is due to loss of water at a temperature considerably below the dry melting point. Cooling is not required.

(iv) *Lack of metallic and troilite chondrules.* Compositions of many chondrules indicate that they would not be completely molten under dry conditions at temperatures below 1600°C. Iron melts at 1539°C. One per cent of carbon (usually present) depresses the solidus below 1400°C. The iron in chondrites is closely associated in the groundmass with troilite, which is miscible in the liquid state with iron. The iron–troilite eutectic is at 1000°C.

Accordingly iron and troilite would be partially or completely molten at temperatures hundreds of degrees below those at which the chondrules are believed to have formed (according to the free drop hypothesis). In chondrites, and also within individual chondrules, iron and troilite do not appear to have ever been molten.* In view of their high surface tensions and immiscibility with silicates, iron and troilite spherules should be produced under any conditions which produce molten silicate drops. Absence of these indicates that chondrule formation occurred

* Very rare occurrences of iron or sulphide "chondrules" have been recorded in the literature. These may well be due to eccentric sectioning of silicate chondrules with iron or troilite rims.

at considerably lower temperatures. According to the model, crystallization temperatures of silicates have been lowered below those of iron and troilite by confined water.

(v) *Occurrence of orthopyroxenes.* The usual pyroxene in chondrules is orthopyroxene, although some clinopyroxene also occurs. If chondrules had crystallized above 1150°C as would occur in free drops, clinopyroxene would have formed (Bowen and Schairer, 1935). The inversion of clinopyroxene to orthopyroxene is extremely sluggish and it is unlikely that it would have occurred in many chondrites which show no evidence of recrystallization and metamorphism, particularly the friable varieties. This would suggest that the chondrules have crystallized below 1150°C. The model attributes this lowering of crystallization temperatures to the presence of confined water in a large body.

(vi) *Occurrence of carbonaceous compounds.* Chondrites often contain small quantities and, rarely, considerable amounts of carbonaceous compounds. These are incompatible with oxidized iron at high temperatures and low pressures. This association is only stable at lower temperatures and under high confining pressures. Occurrence of substantial quantities of water in carbonaceous chondrites and of small amounts of CO, CO_2, H_2, CH_4 and H_2O in most chondrites also suggest crystallization under confining pressure, as in the suggested model.

(vii) *Equilibrium relationships.* Prior's rules, describing systematic oxidation–reduction relationships in chondrites, are indicative of some form of chemical equilibrium, locally attained. In many cases where coexisting olivines and pyroxenes in chondrites have been investigated, the individual minerals are found to be approximately uniform in composition. Furthermore the FeO/MgO ratios in olivines are systematically higher than those in the coexisting pyroxenes.* Such relationships would be expected if they had crystallized in equilibrium from a melt. They are inconsistent with any hypothesis which requires chondrites to be a random mixture of phases of varying composition.

Most stones are found to be brecciated and fragmented. These features are later than chondrule formation and could well have been produced during the cataclysm which shattered the parent planet and during subsequent collisions of fragments. Relative movement of fragments has occurred followed by a degree of compaction. The amount of mixing due to this brecciation has been insufficient to destroy the chemical relationships described by Prior. Therefore the amount of relative movement of fragments has been small, but sufficient to give a visual impression of heterogeneity.

Much of this fragmentation and heterogeneity could have been caused by flowage and convection in the crystal mush of the parent planet during the latest stages of reduction, before complete solidification had set in. Escape of gaseous reduction products and steam at the final stages may also have contributed to the brecciation. The friable nature of many chondrites can be attributed to simultaneous crystallization and loss of water below the dry melting temperature.

Achondrites are considerably rarer than chondrites. Prior (1916) and Urey and Craig (1953) have pointed out that two distinct groups of achondrites

* The significance of this relationship was pointed out to the author by Dr. Harmon Craig.

exist—"chondritic" and "basaltic" types. The former are similar chemically in many ways to the chondrites, and follow Prior's oxidation–reduction rules. Textures of chondrites and achondrites show all degrees of gradation, due to recrystallization of the chondrules, which may finally destroy their identity. This group may therefore be regarded as recrystallized chondrites, or as having formed at temperatures too high to permit chondrule growth, as was previously suggested. No genetic difference is implied.

The "basaltic" group of achondrites may have been derived by processes of fractional crystallization and volatilization operating upon material of chondritic composition. Removal of quantities of olivine and pyroxene from a magma of chondritic composition would leave a residual melt which could produce basaltic achondrites.

4. Average Chemical Composition of Cosmic Non-volatile Material

The basic assumption was made in Section 1 that the ratios of non-volatile components were the same in all planets. The data provided by meteorites and the earth enable these ratios to be determined. The cosmic non-volatile composition will be given by correctly weighting the average silicate and metal fractions of meteorites. The mass ratio of core to mantle in the earth is known, making weighting possible. However the earth and the meteoritic planet occur in different states of oxidation. Therefore the silicate phase of meteorites cannot be directly identified with the earth's mantle A correction must be made before weighting is carried out.

The average composition of the silicate phase of chondrites is set out in Table 4, column 1. The FeO/MgO ratio is 1: 2. In the earth this ratio is close to 1: 5 (Section 5). Meteorites are therefore more highly oxidized than the earth. It is necessary for both to be at the same state of oxidation before weighting can be carried out. Accordingly the FeO/MgO ratio in the average chondritic composition has been reduced to 1: 5 (the excess iron so produced enters the core). The composition for the silicate phase thus obtained (recalculated to 100 per cent) is given in column 2.

However there is now too much SiO_2 in the modified chondrite composition to represent the earth's mantle. Ringwood (1958b) has studied the constitution of the mantle and concluded that olivine is the dominant mineral. This is in accord with most current petrological thought. The modified chondritic composition (column 2) is practically saturated with silica and would crystallize almost completely as pyroxene. In order to produce a reasonable ratio of olivine to pyroxene (about two or three to one) it is necessary to remove about 15 per cent of SiO_2 from the composition given in column 2. The resultant composition, which is now that of the earth's mantle, is given in column 3. According to the initial assumption made, the removal of iron and silicon from the oxidized silicate phase is due to reduction, the products of reduction entering the core as metals. Therefore the silica removed is calculated as silicon and included in the core.

The mass of the core is 30·9 per cent of that of the earth (Bullen, 1953), therefore the overall composition of the earth is found by combining the modified chondrite (column 3) with sufficient nickel–iron to give the required core-to-mantle

Table 4. Composition of earth and chondrites

	1	2	3	4	5	6
SiO_2	47·86	52·99	44·69	30·88	30·88	37·86
MgO	30·00	33·21	39·08	27·00	27·00	23·75
FeO	15·67	6·64	7·81	5·40	5·40	30·99
NiO						2·27
Al_2O_3	3·14	3·48	4·09	2·83	2·83	2·49
CaO	2·45	2·71	3·19	2·20	2·20	1·94
Na_2O	0·88	0·97	1·14	0·79	0·79	0·70
	100	100	100	69·10	69·1	100
Fe		(8·32)	(9·79)	23·20	21·66	
Ni				2·03		
Si			(8·24)	5·67	5·67	
FeS				30·90	(6·48)	

Column 1: silicate phase of average chondritic meteorites (Urey and Craig, 1953).
Column 2: chondrite from column 1 with FeO/MgO ratio reduced to be consistent with the ratio probably occurring in the earth's mantle (1 : 5).
Column 3: chondrite from column 2 with the SiO_2 content reduced by 15 per cent to give a value which provides an acceptable ratio of olivine to pyroxene in the earth's mantle.
Column 4: overall composition of the earth, assuming 69·1 per cent mantle and 30·9 per cent core. Composition of mantle is given by the oxides in column 3. The silica removed in column 3 has been added to the core as metallic silicon. Remainder of core is nickel–iron with average meteoritic ratio 11·89 (Lovering, 1957).
Column 5: average composition of chondrite (Urey and Craig, 1953) with FeO and SiO_2 adjusted as in column 4.
Column 6: completely oxidized non-volatile material of cosmic composition; equivalent to column 4 plus oxygen.

ratio (column 4). This procedure provides the overall chemical composition of the earth, from which the cosmic ratios of non-volatile elements may be derived. The completely oxidized equivalent is given in column 6.

It is of interest to perform a similar operation on the overall composition of chondritic meteorites which contain on the average, 13·2 per cent of dispersed nickel–iron and 5·7 per cent of iron sulphide, in addition to the silicates. By reducing the FeO and SiO_2 contents to values consistent with those in the earth's mantle and adding the extra iron and silicon to the metal phase, the ratio between total metal and silicate is found to be very close to that occurring in the earth (column 5). Therefore the overall composition of chondrites must be very close to the original cosmic non-volatile composition. It follows that the iron meteorites represent a relatively insignificant proportion of the original meteoritic material. The ratio of 35 stones to 1 iron in observed falls (Washington and Adams, 1949) supports this conclusion.

The suggested chemical composition of the earth is set out in column 4. In reconciling the data on meteorites and the earth, the only unusual chemical requirement is that the core should contain about 20 per cent of metallic silicon. In the next section evidence supporting this composition will be described.

5. The Earth

In previous discussions it has been assumed that considerably less oxidized iron occurs in the earth's mantle than in the average chondrite, and that in fact, the FeO/MgO ratio in the mantle is close to 1:5. It is desirable to discuss the justification for this assumption, since important conclusions have been based upon it.

It is well known that the FeO contents of orogenic dunites and olivine bombs in basalts are low, giving an average FeO/MgO ratio of about 1:5. In view of recent geochemical studies (Ross *et al.*, 1954; Ringwood, 1958b) it seems likely that these materials come directly from the upper mantle, thus supporting the above ratio for that region.

Olivine basalts are very common throughout the world and are usually believed to be derived by partial melting of the material in the mantle, at depths ranging down to several hundred kilometres. The earliest olivine to crystallize from these basalts would have been in equilibrium with the olivine in the mantle where fractional melting occurred. The FeO/MgO ratio for the earliest olivines in such basalts is usually close to 1:5. Accordingly the ratio in the mantle from whence they came must be 1:5 or less.

Kimberlites carrying diamonds are known in several countries. They must be derived from depths of at least 120 km (MacDonald, 1954). Kimberlites consist dominantly of olivine together with other components which have apparently been locally concentrated by some differentiation process. The olivine phenocrysts in these kimberlites are magnesia-rich, with FeO/MgO ratios of 1:5 or less (Wagner 1914; Shand, 1934).

It may therefore be concluded from petrological evidence that the FeO/MgO ratio in the outer mantle is unlikely to be higher than 1:5. Further consideration suggests that this ratio holds for the whole mantle. If convection played a part during the crystallization of the mantle, as assumed in the present discussion, then the FeO/MgO ratio will be uniform. On the other hand if fractional crystallization had occurred, then the early ferromagnesians deep in the mantle should contain *less* than is indicated by the 1:5 ratio in the upper mantle.

Finally it may be noted that a content of oxidized iron as high as that occurring in chondrites seems to be ruled out by the work of Birch (1952) on the elasticity of the lower mantle. The relatively small values of the elastic ratio $K\rho$ (K = incompressibility, ρ = density) characteristic of iron silicates severely limits their possible abundance.

Reference has already been made to one requirement of the model—that the earth's core should contain about 20 per cent of silicon. From the composition of the mantle, and from the known phase equilibria, it appears that the minimum temperature at which a moderate amount of liquid could form at the surface is about 1600°C. Higher temperatures would be required at greater depths. This would have been the minimum temperature at which reduction of iron was completed. It may have been substantially higher. Reference to Fig. 1 shows that the iron formed by carbon reduction of a melt containing 45 per cent of SiO_2 at 1600°C would contain 20 per cent of silicon. This amount would increase sharply if the temperature exceeded 1600°C. If, therefore, the earth's core has

been formed by a carbon reduction process, the nickel–iron would inevitably contain substantial amounts of silicon.* Lack of silicon in the metal phase of meteorites is attributed to the lower temperature and intensity of reduction. Because of the higher degree of oxidation in meteorites, liquid forms around 1300°C and iron reduced at this temperature would contain negligible amounts of silicon.

Further evidence supporting the suggestion that silicon occurs in the core is available. Recent work on the density of the core, and the probable density of iron at high pressure (Bullard, 1953, 1957; Birch, 1952) indicates that the material of the core is somewhat less dense than would be expected for iron under the same pressure–temperature conditions. Birch suggests that this may be caused by admixture of light elements, e.g. carbon, silicon and hydrogen, in the core. If the mechanism of core formation suggested herein is correct, silicon is most likely to be present in appreciable quantity.† Birch (1952) has furthermore pointed out that the elastic ratio (K/ρ) of the material in the core appears too high to represent pure nickel–iron. Silicon has an elastic ratio twice that of iron, and a relatively small percentage in the core could provide the required properties.

Under equilibrium conditions, reduction at 1600°C should reduce nearly all iron to metal before appreciable formation of silicon occurred. The fact that some unreduced FeO occurs in the mantle is to be attributed to lack of equilibrium. The intensity of reduction would probably be subject to strong local variations with equilibrium being reached in limited regions at different temperatures and pressures. In some of these, complete reduction to iron containing some silicon may have occurred. In others, reduction would be incomplete, oxidized iron would remain, and the metal phase would carry no silicon. After segregation of the metal from various regions into the core, further convection in the mantle would destroy the heterogeneity and the net result would be a uniform composition containing some oxidized iron. Similarly convection would make the core uniform, with some silicon distributed throughout. The core and mantle would therefore not be in equilibrium. This has some interesting consequences which are examined in Section 6.

6. Electrochemical and Dynamic Effects at the Core–Mantle Boundary

According to the suggested model, an iron alloy is produced by reduction near the surface of the earth. The metal collects into masses which are large enough to sink gravitationally to the core. As the metal sinks, temperature and pressure rise and the chemical equilibrium between alloy and silicates is altered. If the metal has collected into sufficiently large bodies, then attainment of equilibrium, which must take place by diffusion across a phase interface, will become slow relative to the velocity of sinking. Under these conditions the core which is formed is not in chemical equilibrium with the mantle. An analogous effect is exhibited in industrial blast furnaces (Hatch and Chipman, 1949). Disequilibrium between

* MacDonald and Knopoff (1958) have independently concluded that the earth's core contains a substantial amount of silicon.

† Silicon inhibits the solubility of carbon which would probably occur in amounts less than 3 per cent (Greiner *et al.*, 1933)

core and mantle has several interesting consequences. Two equilibria appear most likely to be affected.

(a) *The iron–nickel equilibrium*

When reduction of silicate material containing iron and nickel occurs under low pressure and moderate temperatures, nickel becomes strongly concentrated in the metal phase relative to iron. Meteorites furnish a good example. The analogous reactions:

$$\mathrm{Ni} + \mathrm{FeO} = \mathrm{NiO} + \mathrm{Fe} \quad \text{(Kubaschewski and Evans, 1956)}$$
$$\mathrm{Ni} + \mathrm{FeSiO_3} = \mathrm{NiSiO_3} + \mathrm{Fe} \quad \text{(Zur Strassen, 1930)} \qquad (1)$$

have equilibrium constants around 10^{-2} at 2000°K, again showing that nickel is strongly concentrated in the metal. Increasing pressure displaces the equilibrium, according to the sign and magnitude of the volume change for the reaction:

$$\underset{6{\cdot}59}{\mathrm{Ni}} + \underset{12{\cdot}60}{\mathrm{FeO}} = \underset{10{\cdot}03}{\mathrm{NiO}} + \underset{7{\cdot}10}{\mathrm{Fe}} \qquad \Delta V = -2{\cdot}06 \text{ cm}^3 \qquad (2)$$

$$\underset{6{\cdot}59}{\mathrm{Ni}} + \underset{23{\cdot}48}{\tfrac{1}{2}\mathrm{Fe_2SiO_4}} = \underset{7{\cdot}10}{\mathrm{Fe}} + \underset{21{\cdot}19*}{\tfrac{1}{2}\mathrm{Ni_2SiO_4}} \qquad \Delta V = -1{\cdot}78 \text{ cm}^3 \qquad (3)$$

The magnitudes and signs of these volume changes are a consequence of the smaller size of the Ni^{++} ion compared to Fe^{++} and also of the higher polarizing power of Ni^{++} which further reduces its effective radius in oxy-compounds. As a result, the ΔV calculated for the olivines is probably representative, even if the silicates at the bottom of the mantle are more closely packed polymorphs.

At the core–mantle boundary a pressure of $1{\cdot}37 \times 10^6$ bars obtains (Bullen, 1953). This causes a large amount of compression and would reduce ΔV for reaction (3) by about one-third (Birch, 1952). Accordingly ΔV may be placed at $-1{\cdot}19$ cm^3. It is evident that pressure tends to displace the equilibrium towards the right.

The temperature at the core–mantle boundary (C.M.B.) may be around 4000°K. Zur Strassen (1930) has shown that the equilibrium constant for the analogous reaction (1) increases with rising temperature. It is therefore to be expected that the high temperature at the C.M.B. will also displace the equilibrium towards the right.

The change of free energy ΔF for reaction (3) at the C.M.B. is given by:

$$\Delta F = \Delta F^\circ + RT \ln Q \qquad (4)$$

where ΔF° is the free energy for the reaction of the pure components under the P,T conditions existing at the C.M.B. and Q is the activity quotient of the components at the C.M.B. If it is assumed that the nickel–iron was formed by reduction near the surface of the earth ($P \sim 0$, $T \sim 2000$°K) then Q becomes equal to the equilibrium constant at the surface ($K^{p=0}_{2000}$),

therefore
$$\Delta F = \Delta F^\circ + RT \ln K^{p=0}_{2000} \qquad (5)$$

At the C.M.B.:

$$\Delta F^\circ = -RT \ln K^{p=0}_{4000} + P\Delta V \qquad (6)$$

* Calculated from unit cell dimensions of Ni_2SiO_4 (Taylor, 1930).

where $K_{4000}^{p=0}$ is the equilibrium constant for reaction (3) at 4000°K and zero pressure. Substituting (6) in (5)

$$\Delta F = -RT \ln K_{4000}^{p=0} + P\,\Delta V + RT \ln K_{2000}^{p=0}$$

$$= P\,\Delta V + RT \ln \left(\frac{K_{2000}}{K_{4000}}\right)_{p=0}$$

By extrapolating ZUR STRASSEN's results, $\log \left(\frac{K_{2000}}{K_{4000}}\right)_{p=0}$ is found to approximate $-0{\cdot}40$, P and ΔV are known, $T \sim 4000$°K,

therefore $\Delta F = -163{,}300 - 30{,}600 = -193{,}900$ J ($-46{,}400$ cal)

This result shows that reaction (3) will be displaced very strongly to the right at the C.M.B. As a result, nickel will tend to diffuse from the core to the mantle, and iron will tend to move in the opposite direction. Since the lower mantle possesses a substantial electronic conductivity (RUNCORN, 1955) this disequilibrium sets up an electrolytic cell, causing an e.m.f. at the core-mantle boundary:

$$Ni \rightarrow Ni^{++} + 2e \quad \text{(core)}$$

$$Fe^{++} + 2e \rightarrow Fe \quad \text{(mantle)}$$

Electrons flow from core to mantle, precipitating metallic iron in the mantle, whilst nickel ions diffuse into the mantle. The size of the current and the transfer of material is controlled by the ionic mobility in this region. The e.m.f. of the cell is given by:

$$E = \frac{\Delta F}{n\varepsilon}$$

where ε is the Faraday and n the equivalent number for the reaction, with ΔF as given above.

$$E = 1{\cdot}000 \text{ V}$$

(b) *The silicon–iron equilibrium*

In Section 5 it was suggested that the core contained about 20 per cent of metallic silicon. This gives rise to the equilibrium given in equation (7) below. At ordinary temperatures and pressures, this reaction proceeds strongly to the right. The data are not adequate for prediction of the free energy change at 4000°K. It may not be very large. However there is probably a marked pressure effect, favouring the right hand side:

$$\underset{8{\cdot}96}{Si} + \underset{42{\cdot}05*}{Fe_2SiO_4} = \underset{33{\cdot}70}{2SiO_2} + \underset{14{\cdot}20}{2Fe} \qquad \Delta V = -3{\cdot}11 \text{ cm}^3 \qquad (7)$$

The silicates in the lower mantle are close packed and probably consist essentially of the spinel solid solution Mg_2SiO_4–Fe_2SiO_4 (RINGWOOD, 1958b). The partial molar volume of SiO_2 in such a close packed silicate may be estimated

* This value is the molar volume of Fe_2SiO_4 spinel (RINGWOOD, 1958a).

by subtracting twice the molar volume of FeO from that of Fe_2SiO_4 spinel. This gives a value of 16·85 cm³. The approximate partial molar volume of silicon has been determined from the densities of solid solutions of silicon in α-iron (Greiner *et al.*, 1933). A value of 8·96 cm³ was found. In this manner ΔV for reaction (7) is found to be −3·11 cm³.

At the C.M.B. compression would reduce ΔV to −2·07 cm³, causing a contribution to the free energy of reaction (7) of −283,600 J (−67,780 cal). This would correspond to an e.m.f. of 0·73 V. If the effect of temperature upon reaction (7) had been included, this value might have been somewhat increased. This e.m.f. is

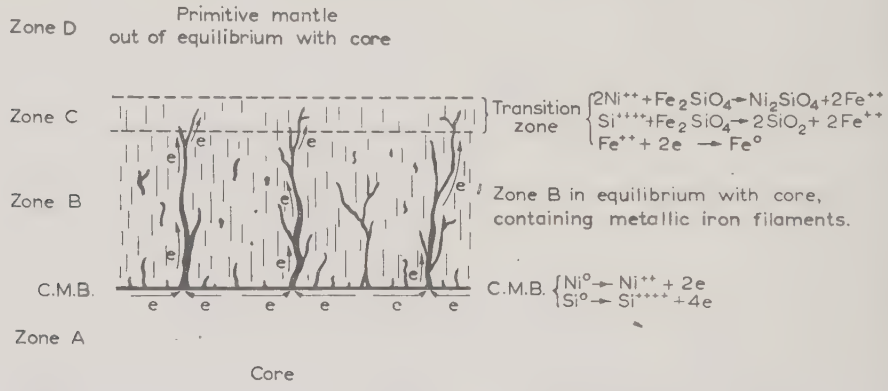

Fig 3. Possible electrochemical effects in vicinity of core–mantle boundary (C.M.B.). Arrows indicate paths of electrons. Vertical stippling indicates paths of cations (upwards). Zone *B* may be a few hundred km wide.

in the same sense as the Ni–Fe e.m.f. with electrons flowing from core to mantle. Metallic iron is precipitated in the mantle, and Si^{++++} ions diffuse from the C.M.B. into the mantle. As in the case of the Fe–Ni cell, the current flowing is governed by the ionic mobility in the lower mantle.

(c) *Possible consequences of an e.m.f. across the core–mantle boundary*

Runcorn (1954) has suggested that an e.m.f. of about 1 V across the C.M.B. would explain the core–mantle coupling required to explain rapid changes in the length of the day. He further suggested that this e.m.f. might be the ultimate source of the earth's magnetic field. Runcorn suggested that the e.m.f. was of thermoelectric origin, but this view has been criticized (Bullard, 1954). The electrolytic e.m.f.'s discussed in the previous sections are of the required size and may be able to cause the effects discussed by Runcorn.

Possible types of current systems which could be caused by these electrolytic e.m.f.'s may be considered—Figs. 3 and 4. In the mantle nearest to the core (zone *B*), chemical equilibrium will have been reached between core and mantle. Accordingly this zone will contain substantial amounts of metallic iron which have been replaced by Ni and Si diffusing from the core. This zone grades upwards through transition zone *C* into the unmodified mantle (zone *D*) which is out of equilibrium with the core with respect to Ni and Si. These elements are presently

diffusing into zone D from the core under the influence of the potentials previously calculated.

At the C.M.B., Ni and Si atoms in the core become ionized and enter zone B.

$$\overset{\circ}{\mathrm{Ni}} \rightarrow \mathrm{Ni}^{++} + 2e$$

$$\overset{\circ}{\mathrm{Si}} \rightarrow \mathrm{Si}^{++++} + 4e$$

The ions and elections migrate towards zone D by different mechanisms—the ions by diffusion and the electrons by electronic conduction [the lower mantle is a reasonably good electronic conductor (RUNCORN, 1955)]. On arrival in region D

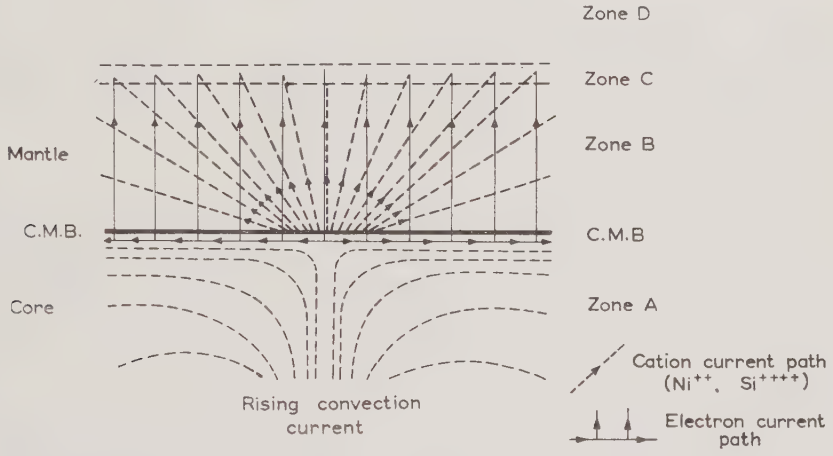

Fig. 4. Possible current system in C.M.B. region in neighbourhood of rising convection current. For further details, refer to Fig. 3 and text.

the electrons precipitate Fe^{++} as metallic iron, which is replaced in the silicates by an equivalent amount of Ni^{++} and Si^{++++}.

Accordingly a current of positive ions accompanied by an equivalent current of electrons flows outwards radially from the core. If the mantle is completely homogeneous in electrical properties, the positive and negative currents neutralize each other, giving rise to zero resultant current. Such a situation is unlikely, however. Zone B contains a large amount of precipitated iron which may in places form a conductor between regions A and D. Since the electronic conductivity of iron is much higher than the silicates of the mantle, the electrons will be preferentially carried by the iron—thus giving rise to heavy localized electronic currents, whilst the cation current is diffuse and evenly distributed throughout the whole region. Where these metallic conductors meet the core, electron currents parallel to the C.M.B. will occur. Directions of these are indicated by the arrows in Fig 3.

Formation of the localized scattered iron conductors in zone B may be directly due to the nature of the electrolytic interaction governing precipitation of the iron. An analogy is provided by dendrite formation between the electrodes of electrolytic cells. Precipitation of metal on an electrode may form a random protuberance. This

receives a high charge density and consequently further precipitation of metal occurs preferentially on this region at the expense of the surrounding area. As a result the protuberance grows outwards as a dendrite, towards the opposite electrode. Eventually it reaches it and causes a short circuit. Heavy current flows along the dendrite and may cause it to burn out.

Currents may also be produced by another mechanism (Fig. 4) dependent upon the occurrence of convection currents in the core. It will be assumed that:

(1) The current systems are large and simple, with no turbulence or secondary currents.

(2) Ni^{++} and Si^{++++} diffuse more rapidly through the mantle (zone *B*) than Ni and Si diffuse in the core.

In support of assumption (2) it is pointed out that ions in the mantle are diffusing along a strong potential gradient (calculated in previous sections) whereas in the core the atoms are diffusing along a weak concentration gradient.

If these assumptions are accepted we find that the electrolytic action becomes concentrated around the loci of ascending convection currents (Fig 4). As an ascending current containing average quantities of $\overset{\circ}{Ni}$ and $\overset{\circ}{Si}$ comes in contact with the C.M.B., these elements become ionized and enter the mantle. As the currents turn over and flow parallel to the C.M.B., a thin region of the current nearest to the C.M.B. becomes depleted in Ni and Si and the rate of entry of these elements decreases. Most of the Si^{++++} and Ni^{++} enter the mantle at the loci of ascending currents where the supply of these elements at the surface is constantly replenished.

The ions diffuse by direct paths to reach zone *D* as is indicated by Fig. 4. However the electrons follow the course of smallest electrical resistance to zone *D*. Since the core is a good electronic conductor, they flow parallel to the C.M.B. and then vertically upwards by the shortest path, as indicated on Fig. 4. Thus the rising convection currents are also the centre of outwardly directed electronic currents which flow parallel to the C.M.B. The resultant current system resembles that suggested by Runcorn (1954) to be maintained by thermoelectric e.m.f.'s.*

If the rate of ionic diffusion is sufficiently large, some important effects occur. Migration of nickel and silicon into the lower mantle causes the proportion of iron in the core to rise. This may result in precipitation of solid iron, to which the inner core could be attributed. According to this view, the inner core has been growing over geological time owing to electrolytic precipitation. Crystallization of iron on the inner core causes latent heat evolution and therefore increases the temperature. This may cause convection. By this mechanism, crystallization of iron at the inner core continues despite liberation of heat and rise in temperature, due to withdrawal of low melting components of the liquid core at the C.M.B.

Migration of silicon into the mantle may result in a sufficient increase in the density of the residual liquid metal near the C.M.B. to cause convection also.

* The writer wishes to acknowledge the value of helpful discussions with Dr. W. R. Joyner (Harvard) and Dr. J. O'M. Bockris and Dr. A. Despic of the University of Pennsylvania, which have influenced the treatment of the preceding section. In particular, the analogy between dendrites in electrolytic cells and precipitation of iron in zone *B* was suggested by Dr. Despic.

Finally, liquid iron which is electrolytically precipitated in the lower mantle might settle out in some manner (e.g. UREY, 1952). Because of its purity it would probably be denser than the liquid in the core and sink towards the inner core where it would precipitate.

It is therefore conceivable that the electrolytic process suggested might be responsible both for the primary e.m.f. and for the maintenance of convection in the core. Previous suggestions (BULLARD, 1953) requiring radioactive heat sources in the core to maintain convection leave much to be desired.

The diffusional effects in the lower mantle, and precipitation of iron, should produce modification of seismic velocities in this region. JEFFREYS (1939) and GUTENBERG (1948) have published velocity curves showing a marked flattening in the velocity gradients in the mantle near the core boundary.

The electrolytic reactions discussed proceed with decrease in volume—indeed this is the principal reason for their existence. They may therefore make a significant contribution to the contraction of the earth.

7. Densities of the Planets

In Section 2(a) it was pointed out that the density of planets will increase as the degree of reduction increases. This effect is illustrated in Fig. 2. It therefore becomes possible to interpret the varying densities of planets as due to varying degrees of reduction of primitive non-volatile material.

(a) *Venus.* UREY (1952) in a recent discussion selects 4·87 g/cm^3 as the best value of the mean density of Venus. KUIPER (1952) has suggested 5·06 g/cm^3. The mass of Venus is 0·8136 of the earth. When allowance for compression and polymorphic changes is made the uncompressed density of Venus would be close to that of the earth. As UREY (1952) has pointed out, the two planets are so similar that practically any hypothesis of density distribution and origin would fit both equally well. Accordingly the density of Venus may be accounted for by assuming a state of oxidation similar to that occurring in the earth.

(b) *Mercury.* Estimates of density for this planet vary widely. UREY (1952) gives two possible values: 4·58 g/cm^3 and 5·05 g/cm^3. KUIPER (1952) suggests 5·46 g/cm^3. Individual determinations of mass and radius are given with relatively small margins of error and it therefore seems that systematic errors of some sort are occurring. For the present discussion a value of $5 \pm 0{\cdot}5$ g/cm^3 would be consistent with variations cited.

A high degree of reduction of the primitive material would be necessary to produce these densities. Reference to Fig. 2 shows that the lower limit (4·4 g/cm^3 uncompressed) would require total reduction of iron and about 70 per cent reduction of silicon. By complete reduction of silicon, the uncompressed density rises to 4·80 g/cm^3—equivalent to about 4·95 g/cm^3 under the self-compression likely to exist in Mercury.

Complete reduction of silicon requires a temperature in the vicinity of 2000°C. Before this temperature is reached MgO becomes reduced to magnesium vapour. Since the escape energy on Mercury is low, and the temperature high, the Mg vapour may escape by evaporation, leading to an increased density for the residual material. If future determinations should definitely indicate a density higher than

5 for Mercury, a volatilization process of this type would be adequate. Volatilization of Mg would be a necessary consequence of a high reduction temperature, and does not require any further assumption.

(c) *Mars.* Urey (1952) suggests values of 3·96 and 4·24 g/cm^3 for the density of Mars; Kuiper's value is 4·12 g/cm^3. The density of completely oxidized non-volatile primitive material (Fig. 2) is 3·57 g/cm^3. When allowance is made for the compression of Mars and probable phase changes in silicates, this would be increased to 4·09 g/cm^3. This is close to the astronomical values. According to the model therefore, Mars would be regarded as primitive non-volatile material which had suffered no subsequent reduction. A possible reason for this could be that no carbonaceous material collected with the dust when Mars was formed, due to the local conditions of accumulation.

Urey has pointed out that Mars is approximately homogeneous and probably does not possess a core. This is consistent with the interpretation offered.

(d) *The meteoritic planet.* The density of the original meteoritic planet can be obtained from Fig. 2, since the degree of oxidation is known. It is found to be 3·77 g/cm^3. From the data in Section 4, the meteoritic planet is found to contain 17 per cent of nickel–iron.

(e) *The outer planets.* Jupiter, Saturn, Uranus, Neptune and Pluto all possess low densities. These are probably due to retention of large amounts of the original volatile materials (Kuiper, 1952). Gas escape by evaporation during planetary accumulation has apparently been incomplete.

(f) *The moon.* The mean density of the moon is 3·33 g/cm^3 This is significantly lower than the density of oxidized primitive non-volatile material (3·57 g/cm^3). This suggests that some volatile material of low density may occur on the moon, e.g. water and carbonaceous compounds. Three per cent of water would reduce the density of oxidized primitive material to 3·33 g/cm^3. The water would probably occur as hydrated silicates, concentrated towards the periphery. Radioactive generation of heat has probably driven off most of the original water which may have been present in the central regions. Urey (1952) has also concluded that the moon consists essentially of oxidized primitive material.

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References

Birch F. (1952) *J. Geophys. Res.* **57,** 227.

Birch F. (1958) *Bull. Geol. Soc. Amer.* **69,** 483.

Bowen N. L. and Schairer J. F. (1935) *Amer. J. Sci.* **29,** 151.

Brown H. and Patterson C. (1948) *J. Geol.* **56,** 85.

Bullard E. C .(1953) *The Earth as a Planet* (Edited by Kuiper G. P.), Ch. 3. Chicago University Press.

Bullard E. C. (1957) *Verh. Geol.-mijnb. Genoot. Ned. Kolon.* **18,** 23.

Bullen K. E. (1953) *Introduction to the Theory of Seismology,* p. 219. Cambridge University Press.

Dufay J. (1957) *Galactic Nebulae and Interstellar Matter*. Hutchinson, London.
Farrington O. C. (1901) *J. Geol.* **9**, 174; 393; 522.
Fulton J. C. and Chipman J. (1954) *J. Metals, N.Y.* 1136.
Greiner E. S., Marsh J. S. and Stoughton B. (1933) *The Alloys of Iron and Silicon*, Ch. 7-8. McGraw-Hill, New York.
Gutenberg B. (1948) *Bull. Seismol. Soc. Amer.* **39**, 121.
Hatch G. G. and Chipman J. (1949) *J. Metals, N.Y.* **1**, 274.
Hopkins D. W. (1954) *Physical Chemistry of Metal Extraction*. Garnet Miller, London.
Jeffreys H. (1939) *Mon. Not. R. Astr. Soc. Geophys. Suppl.* **4**, 498.
Kohman T. P. and Saito N. (1954) *Ann. Rev. Nucl. Sci.* **4**, 401.
Kubachewshi O. and Evans E. L. (1956) *Metallurgical Thermochemistry*. Pergamon Press, London.
Kuiper G. P. (1952) *The Atmospheres of the Earth and Planets*, Ch. 12. Chicago University Press.
Kuiper G. P. (1955) *J. R. Astr. Soc. Can.* **50**, 57.
Latimer W. M. (1950) *Science* **112**, 101.
Lawson D. W. and Jamieson J. C. (1958) *J. Geol.* **66**, 540.
Lovering J. F. (1957) *Geochim. et Cosmochim. Acta* **12**, 253.
MacDonald G. J. F. (1954) Ph.D. Thesis, Harvard University.
MacDonald G. J. F. and Knoppoff L. (1958). In press.
Prior G. T. (1916) *MinerMag.* **28**, 26..
Richardson F. D. and Jeffes J. H. E. (1948) *J. Iron St. Inst.* **160**, 261.
Ringwood A. E. (1958a) *Bull. Geol. Soc. Amer.* **69**, 129.
Ringwood A. E. (1958b) *Geochim. et Cosmochim. Acta* In press.
Ross C. S., Foster M. D. and Myers A. T. (1954) *Amer. Min.* **39**, 693.
Rubey W. W. (1955) Crust of the Earth, p. 631 *Spec. Pap. Geol. Soc. Amer.* 62.
Runcorn S. K. (1954) *Trans. Amer. Geophys. Un.* **35**, 49.
Runcorn S. K. (1955) *Trans. Amer. Geophys. Un.* **36**, 191.
Shand S. J. (1934) *Trans. Geol. Soc. S. Afr.* **37**, 57.
Strassen Zur H. (1930) *Z. anorg. Chem.* **191**, 209.
Taylor N. W. (1930) *Z. phys. Chem.* 241.
Urey H. C. (1952a) *The Planets*. Yale University Press, New Haven.
Urey H. C. (1952b) *Geochim. et Cosmochim. Acta* **2**, 263.
Urey H. C. (1953) *Proc. Roy. Soc.* A **219**, 281.
Urey H. C. (1954) *Astrophys. J.* Suppl. Ser. 1, 147.
Urey H. C. (1955) *Proc. Nat. Acad. Sci., Wash.* **41**, 127.
Urey H. C. (1956) *Astrophys. J.* **124**, 623.
Urey H. C. (1957) *Physics and Chemistry of the Earth*, Vol II, Ch. 3. Pergamon Press, London.
Urey H. C. and Craig H. (1953) *Geochim. et Cosmochim. Acta* **4**, 36.
Urey H. C. and Donn B. (1956) *Astrophys. J.* **124**, 307.
Von Weizsacker C. F. (1944) *Z. Astrophys.* **22**, 319.
Wagner P. A. (1914) *Diamond Fields of South Africa*, Ch. 2.
Washington H. S. and Adams L. H. (1949) *Internal Constitution of the Earth* (Edited by Gutenberg) Ch. 5, Dover Publications, New York.
Wiik H. B. (1956) *Geochim. et Cosmochim. Acta* **9**, 279.

Geochimica et Cosmochimica Acta, 1959, Vol. 15, pp. 284 to 304. Pergamon Press Ltd. Printed in Northern Ireland

Distribution of Li, Na, K, Rb, Cs, Pb and Tl in southern Norwegian pre-Cambrian alkali feldspars

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Abstract—The concentrations of Li, Rb, Cs, Pb and Tl have been determined spectrographically and Na and K by flame photometer in eighty-eight feldspars from the pre-Cambrian basement rocks of southern Norway. Rock types include gneisses, augengneisses, anatexe granites, diapire (post-orogenic) granites and small and large pegmatites. Analytical procedures are described.

Normal K/Rb ratios are found except for those from some large pegmatite feldspars which are enriched in Rb, and feldspars from arendalites which are relatively impoverished. The latter effect is shown to be related to feldspar structure and bulk composition. Changes in the K/Rb ratio are traced with increasing differentiation in the Fevig diapire granite. Feldspars from small pegmatites are similar in composition to the country rock. Those from large pegmatites fall into three compositional groups.

The trace element content of the feldspars seems in general to reflect the differences in geological conditions under which they were formed.

1. Introduction

The problems of pre-Cambrian geology are diverse and frequently not amenable to treatment by classical geological methods. This is reflected in the term "basement complex" used to cover the assortment of gneisses, augengneisses, migmatites, granites of one origin or another and pegmatites of various sizes. The one common feature agreed on by most workers is that the rocks have been recrystallized during conditions ranging from high grade metamorphic to magmatic. It was felt that a useful approach would be to establish the trace element distribution in one of the common and ubiquitous phases, the alkali feldspars, and to see if significant differences could be established and correlated with the geological conditions under which they crystallized. Recent advances in the quality of geochemical data have made it possible to use certain trace elements in this manner.

This is the second paper of a series investigating the trace element composition of feldspars from the pre-Cambrian basement complex of southern Norway (Fig. 1). The general geological setting has been described in our first paper (Taylor and Heier, 1958). In the summer of 1957, we collected additional samples from a wide area. In our first paper we reported determinations of the alkali elements only. In this paper, we include data on lead and thallium (including the samples from Taylor and Heier, 1958). Work is in progress on the determination of Ca, Sr and Ba and some preliminary results are given in this paper.

2. Sample Preparation and Analytical Methods

Mineral separations were in general carried out as described previously. The alkali feldspars (nos. 5, 18, 21 and 36–43)‡ from several granites and gneisses were large enough to be separated by handpicking.

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‡ All sample numbers in the text refer to Table 1. Localities are given in Table 7 and indicated on the map Fig. 1.

Determination of the alkali metals

The procedures were similar to those described in our previous paper with minor modifications. Anodes having an internal diameter of 2·4 mm and a depth of 2·5 mm were substituted for the narrower deeper electrodes previously used. They were more satisfactory because the molten bead of involatile elements (formed during arcing of unmixed samples at low currents) was much more stable and was almost always retained until the alkali metals had completely distilled. National Carbon Co. special graphite (anodes) and carbon (cathodes) were used.

Potassium was used as the internal standard, the pairs Li 6707/K 6939 and Rb 7947/K 6939 being used. For caesium, the pair Cs 8521/K 6939 was used. Relative deviation (per cent standard deviation) was 3 per cent for Rb and 5 per cent for Li and Cs.

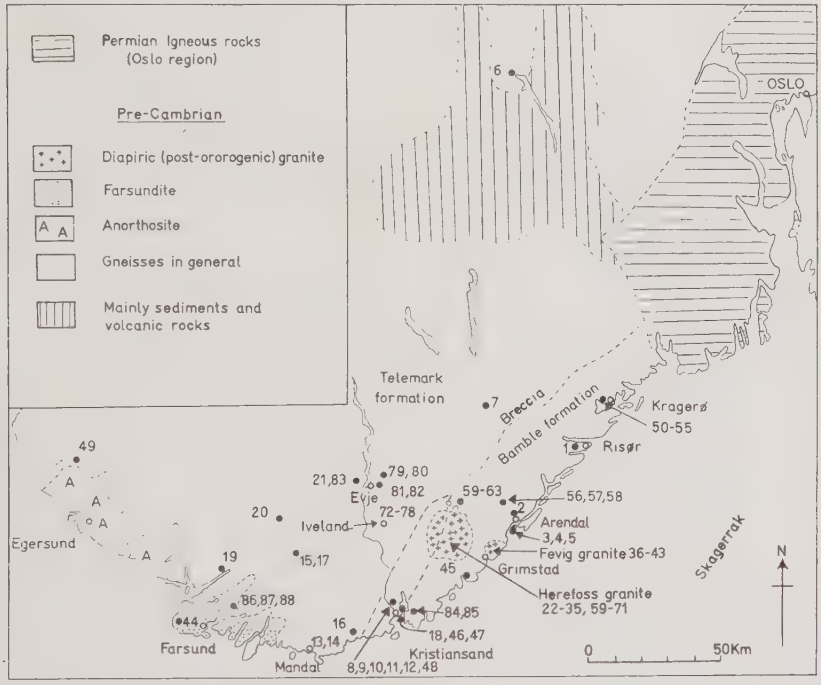

Fig. 1. Geological sketch map of southern Norway showing sample localities.

G-1 and W-1 were again used as basic standards for Li and Rb with the same values as given in Taylor and Heier (1958). No adequate silicate standards for Cs were available in our laboratory until Smales and Cabell (1957) published Cs determinations using neutron activation analysis for the intercalibration suite of lepidolites. The lepidolite from Bob Ingersoll Mine, South Dakota (A-106) (containing 1440 p.p.m. Cs) was mixed with a feldspar from Kragerø (no. 52) which had a very low Cs content (1·1 p.p.m.) and a series of standards of various dilutions was prepared in the usual way. The Cs figures given in our previous paper, (Taylor and Heier, 1958) are based on these standards. Na and K were determined by flame photometer.

Determination of Pb *and* Tl

Samples were arced at low current until the end of the alkali metal distillation phase. Conditions were as follows: Hilger large quartz and glass spectrograph. Quartz optics; Wavelength range 2750–4680 Å; Ilford ordinary (N. 30) plate; Slit 20 μ; 7 step sector (2 : 1 ratio); Lower electrode (anode) National Carbon Co. special graphite 2·4 mm int. diam. × 5 mm depth; Upper electrode (cathode) National Carbon Co. special carbon 3·2 mm ($\frac{1}{8}$ in.) diam. The unmixed samples were arced at 4·4 A d.c. Plates were developed in Kodak D-19b for 5 min.

Table 1. Analyses of alkali feldspars

Sample no.	Rock type	Li p.p.m.	Na %	K %	Rb p.p.m.	Cs p.p.m.	Pb p.p.m.	Tl p.p.m.
	A. Bamble formation							
1	Sillimanite granite	0·5	0·39	12·27	285	Tr	1·2	—
2	Arendalite	1·7	2·95	5·37	77	—	—	—
3	Arendalite	1·4	4·28	5·77	98	—	—	—
4	Arendalite	2·9	3·27	5·89	46	—	5·4	—
5	Gneiss	—	3·52	7·51	185	—	13	8·8
	B. Telemark formation							
6	Tinngranite	1·1	1·77	10·54	500	16	9·7	2·7
7	Telemark granite	1·2	1·89	9·55	235	—	14	2·5
8	Anatexe granite	2·8	1·13	11·59	770	38	18	—
9	Oddersjå (Anatexe granite)	3·7	0·98	12·15	860	15	17	25
10	Oddersjå (Anatexe granite)	2·6	0·91	11·80	740	—	12	30
11	Oddersjå (Anatexe granite)	16	0·98	12·09	360	—	37	2·5
12	Oddersjå (Anatexe granite)	0·9	0·82	12·38	910	9·2	9·5	7·1
13	Holum granite	1·6	1·41	11·21	570	2·3	12	5·5
14	Holum granite	2·2	1·56	10·80	530	1·9	18	6·4
15	Gneiss granite	5·8	0·94	11·90	750	16	6·2	5·4
16	Gneiss	5·1	1·69	7·94	500	2·7	22	—
17	Gneiss	2·2	0·89	12·25	690	3·1	11	5·3
18	Augengneiss	1·2	1·80	9·65	340	—	14	7·9
19	Augengneiss	12	2·14	9·72	320	—	38	—
20	Augengneiss	6·2	2·64	8·85	450	—	28	—
21	Augengneiss	0·7	2·16	9·33	160	—	19	1·9
22	Augengneiss	0·6	1·91	9·90	240	—	7·4	—
23	Gneiss	0·3	0·86	12·49	550	Tr	18	12
24	Gneiss	1·6	1·04	12·50	510	—	25	7·2
25	Granitic gneiss	0·3	0·67	12·62	575	—	—	5·8
	C. Herefoss (diapire) granite							
26	Granite	0·3	0·93	12·22	400	—	3·1	2·1
27	Fine-grained granite	0·5	1·69	10·49	330	—	3·7	8·0
28	Coarse granite	0·2	1·27	11·69	460	—	11	6·6
29	Coarse granite	0·8	1·47	11·13	305	—	10	3·5
30	Coarse granite	0·2	1·57	11·16	300	—	11	4·0
31	Coarse granite	0·9	1·74	10·85	300	—	12	1·3
32	Coarse granite	1·3	1·77	9·83	450	Tr	11	7·9
33	Granite	1·5	2·40	9·47	390	—	13	2·6
34	Fine-grained granite	1·3	0·88	12·74	350	Tr	16	5·9
35	Granite	2·1	0·91	12·76	420	24	28	12
	D. Fevig (diapirie) grante							
36	Granite	—	2·92	8·25	210	—	21	1·6
37	Granite	1·1	3·15	7·92	190	—	28	1·7
38	Granite	1·1	2·82	8·72	180	—	25	1·4
39	Granite	1·9	2·65	8·75	330	—	19	2·6
40	Granite	0·1	2·60	9·09	370	—	17	2·3
41	Granite	0·6	2·63	8·78	290	—	23	1·8
42	Granite	1·3	2·79	8·55	210	—	47	2·4
43	Red granite vein in gneiss	1·4	3·13	7·56	290	—	33	2·0
	E. Farsundite							
44	Granite	5·1	1·74	10·94	1100	3·4	5·6	8·2

Table 1.—(*contd*)

Sample no.	Rock type	Li p.p.m.	Na %	K %	Rb p.p.m.	Cs p.p.m.	Pb p.p.m.	Tl p.p.m.
	F. Small pegmatites							
45	Vein in gneiss	—	1·37	11·27	280	Tr	6·3	7·7
46	Vein in augengneiss	0·5	1·21	10·50	330	—	19	7·2
47	Vein in augengneiss	—	1·62	10·96	420	—	17	—
48	Vein in Oddersjå granite	4·5	1·90	10·89	640	1·9	38	6·7
49	Vein in gneiss	3·7	2·27	9·58	500	—	16	7·0
	G. Large Pegmatites							
	Name							
50	Kalstad, Kragerø	0·5	2·14	9·94	510	2·7	3·0	13
51	Kalstad, Kragerø	0·8	2·45	9·55	840	3·8	4·9	33
52	Lindvikskollen, Kragerø	0·2	2·11	10·52	610	1·1	2·0	3·0
53	Lindvikskollen, Kragerø	0·3	2·40	10·06	550	1·9	—	6·7
54	Tangen, Kragerø	0·1	2·46	10·09	880	14	—	3·2
55	Tangen, Kragerø	0·4	2·73	9·01	740	8	—	5·7
56	Gloserhei, Arendal	0·1	2·06	10·30	640	0·8	—	2·6
57	Gloserhei, Arendal	0·1	1·91	10·58	620	1·5	—	4·8
58	Gloserhei, Arendal	0·1	2·11	10·65	790	1·5	—	11·6
59	Hinnebu Aust-Agder	2·0	1·51	11·04	1400	13	41	18
60	Hinnebu Aust-Agder	3·1	1·68	11·19	1400	15	39	18
61	Lauvrak Aust-Agder	1·5	1·39	11·44	1600	23	54	22
62	Lauvrak Aust-Agler	0·3	1·29	11·65	2000	25	50	16
63	Øygardstj Aust-Agder	2·0	1·77	11·16	560	11	33	—
64	Herefoss	1·1	1·50	11·39	695	16	41	9·6
65	Herefoss	0·6	2·08	10·74	750	22	27	6·8
66	Begervann	0·7	1·41	11·55	700	7	13	9·6
67	Åmli	1·8	1·51	11·29	690	8	20	7·1
68	Stie	—	1·94	11·07	810	—	34	11
69	Stie (Amazonite)	0·7	1·91	10·87	1340	30	38	46
70	Krossöl	0·8	1·94	10·79	550	—	14	8·4
71	Valbeland	0·6	2·45	9·96	480	—	19	7·3
72	Eretveit, Iveland	0·1	1·72	10·89	790	6·1	39	12
73	Eretveit, Iveland	0·1	1·90	10·78	630	5·7	42	2·0
74	Tuftan, Iveland	3·7	2·22	10·42	1230	11	97	11
75	Tuftan, Iveland	3·1	2·07	10·66	1150	11	115	10
76	Mannekleiv, Iveland	—	1·14	11·54	760	18	43	5·2
77	Heia, Iveland	—	2·57	9·96	960	18	60	18
78	Knutten, Iveland	—	2·38	10·00	1020	36	95	120
79	Uranium Mine, Evje	1·6	2·41	9·85	570	—	92	14
80	Uranium Mine, Evje	—	2·37	10·09	500	—	160	35
81	Flåt, Evje	—	1·78	10·46	660	23	89	13
82	Flåt (Amazonite), Evje	—	1·26	11·72	1730	700	54	140
83	Ås, Evje	1·0	1·97	10·13	280	—	42	2·8
84	Varoddbrua, Kristiansand	0·5	1·78	10·87	1200	100	6	43
85	Varoddbrua, Kristiansand	0·8	1·82	10·58	825	36	7	32
86	Rømteland 1	4·2	1·36	11·55	3400	100	75	63
87	Rømteland 2	2·0	2·32	10·60	2300	44	110	53
88	Rømteland 3	4·6	2·16	10·60	1400	10	61	18

— not detected

Sodium was used as a variable internal standard, Na 3303 being used. The analysis lines were Tl 3775 and Pb 4057. Relative deviation calculated at 5 per cent.

G-1 and W-1 were used as basic standards for lead. Two feldspars kindly supplied by Dr. D. Shaw, and containing 21 and 84 p.p.m. Tl served as basic Tl standards. Working curves based on synthetic standards for Pb and Tl were displaced from curves based on the above standards.

Determination of Ca, Sr *and* Ba

These elements are much more involatile in the d.c. arc than the alkali elements. Samples were mixed with a graphite palladium mix and arced at a high amperage thus keeping selective distillation to a minimum. Conditions were as follows: Hilger large quartz and glass spectrograph. Glass optics; Wavelength range 3800–5300 Å; Ilford Ordinary (N. 30) plate; Slit 10 μ; 7 step sector (2 : 1 ratio); Lower electrode (anode) National Carbon Co. special graphite; 2·4 mm int. diam. × 5 mm depth; Upper electrode (cathode) National Carbon Co. special carbon 3·2 mm ($\frac{1}{8}$ in.) diam. Current 6·8 A d.c.; 50 mg sample was mixed with 250 mg of the graphite-Pd mix. This consisted of nine parts graphite (prepared from Ca-free National Carbon Co. special graphite electrodes) and one part of $[(NH_3)_4Pd](NO_3)_2$.

Lines used were Ca 4454·78, Sr 4607, Ba 4934, with Pd 4473 as the internal standard line. No interference on Ca 4454·78 was observed from Fe 4454·4 or Ti 4455·3 except in W-1 which was thus not used as a Ca standard.

G-1 and W-1 served as basic standards for Sr, and Ba and G-1 for Ca. Development of this method and evaluation of precision are in progress.

Discussion of Analytical Data

Lithium. The potash feldspars are very low in Li, averaging 1 p.p.m. of those containing Li. As was the case in our previous paper, the feldspars from the large pegmatites are particularly low in Li and in many it was below detection limit. The highest value in Li (2·9 p.p.m.) comes from the feldspar from an arendalite (no. 4). These figures indicate that the occasional high figures reported by us previously were probably due to contamination. In the present case, all samples where contamination by mica was possible were cleaned by magnetic separation. In the Fevig granite, Li shows a general inverse relation with rubidium (see under discussion on Rb), decreasing towards the centre of the granite.

Rubidium. As was the case in our previous paper, we have plotted K(%) and Rb (p.p.m.) on the figure due originally to Ahrens *et al.* (1952). The limits of scatter on Ahrens' diagram are indicated, and since these have been confirmed by many additional analyses (Ahrens, 1954a; Taylor *et al.*, 1956) are taken to indicate the limits of normal K/Rb ratios. Samples whose K/Rb plot lies outside these limits are considered to have anomalous or abnormal K/Rb ratios. This distinction is thought to be valid, so long as the two conditions of adequate precision and satisfactory accuracy are attained in the determination of K and Rb. With the current analytical procedures, adequate precision can be taken as a relative deviation of less than $\pm$5 per cent. Accuracy must be controlled by calibration with G-1 and W-1. With reliable data of this sort, variations from the well-established K/Rb coherence have geological significance.

Normal K/Rb ratios are shown by all the feldspars with the exception of two distinctive types. (a) Some feldspars from large pegmatites show enrichment in Rb and (b) feldspars from the Arendalite (= Charnockite) of the Bamble formation show impoverishment in Rb. These anomalies will be discussed later.

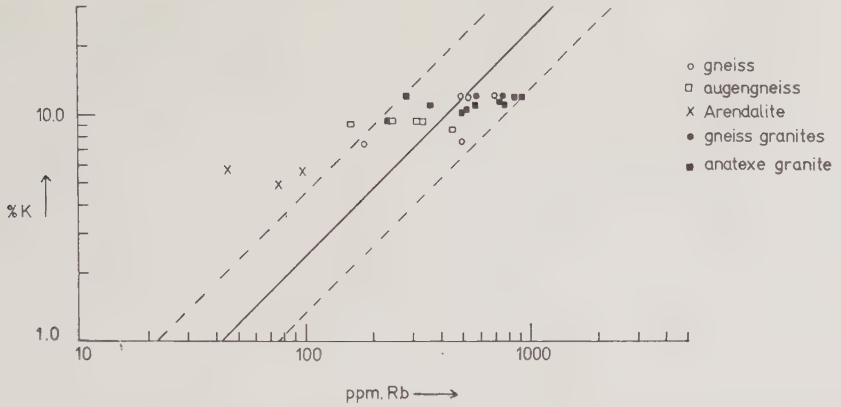

Fig. 2. K/Rb relationship for feldspars from the basement gneisses and granites superimposed on AHRENS *et al.* (1952) K/Rb curve. For parallel displacement of curve, see TAYLOR *et al.* (1956). Dashed lines indicate limits of normal scatter.

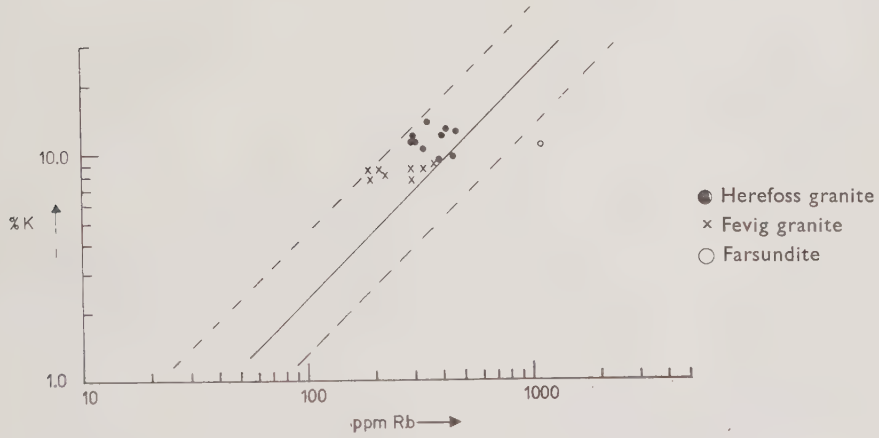

Fig. 3. K/Rb relationship for diapire (post orogenic) granites.

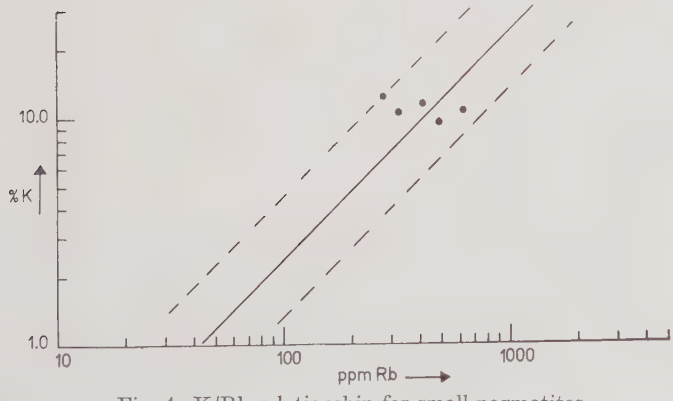

Fig. 4. K/Rb relationship for small pegmatites.

The basement gneisses and granites, of which we have samples mainly from the Telemark formation, show normal ratios. These are plotted in Fig. 2. No trends can be discerned separating the various rock types. Augengneisses tend to be low in Rb, but there are not enough samples to establish this trend.

The overall metamorphic processes to which the "basement" has been subjected involving temperatures of at least 400°C do not seem to have affected K/Rb coherence. The small pegmatites* occurring in the gneisses (see Fig. 4) are frequently, but not universally, conformable. They have been held to be the result of many processes, involving the whole range of magmatic and metamorphic activity

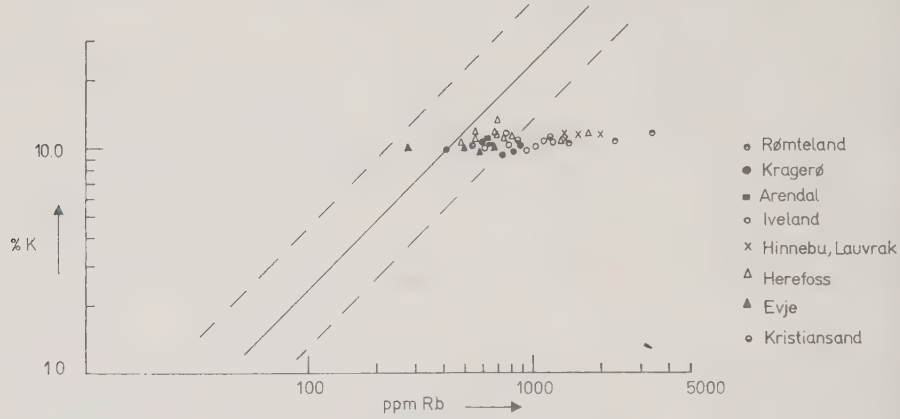

Fig. 5. K/Rb relationship for large pegmatites.

(see Ramberg, 1956). They show comparable K/Rb ratios with the rocks in which they occur and have not been subjected to any process extreme enough to cause Rb to be differentiated from K. This is also the case for some large pegmatites, but not for others.

Post orogenic (diapire) granites

Both the Fevig and Herefoss granites show interesting relationships. They are intrusive into the surrounding gneisses, often with sharp contacts, and are rather uniform in composition. Fig. 6 shows a map of the Fevig granite (mainly from Oftedal, 1937) and shows the variation in K and Rb across the granite. K shows a slight rise towards the centre (presumably the last part to crystallize) but Rb shows a much more pronounced rise so that the K/Rb ratios decrease. If the Fevig granite crystallized from the outside towards the centre, here we have a clearly established enrichment in Rb as differentiation proceeds. Such trends although indicated have not been fully established before.

Tauson and Stavrov (1957) indicate a four-fold increase in Rb in the last formed granites of the Susamyr batholith. No K figures are given.

Sample no. 43 is from a granite vein in the gneiss immediately south-west of the Fevig granite contact. The feldspar is identical in appearance to the microclines of the granite. The K/Rb ratio corresponds to that of the central (most differentiated)

* By the term "small pegmatites" we refer to veinlets and lenses endemic in the gneiss.

part of the granite, and indicates the late origin of the vein. (The sample is contaminated with plagioclase but this will not upset the K/Rb ratio, merely increasing the Na content. No. 37 is probably likewise contaminated.)

The case is not so clear for the Herefoss granite. In the area east of the breccia (samples 32. 33) the K/Rb ratios are lower. This difference may reflect post-intrusive uplift of the eastern half of the granite relative to the western. The appendix

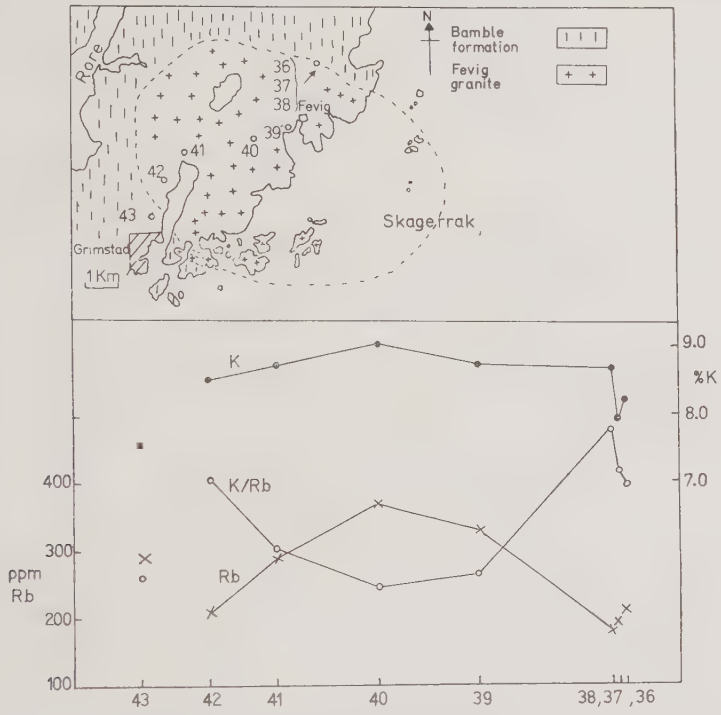

Fig. 6. (a) Geological sketch map of the Fevig granite, showing sample localities (map after Oftedal, 1937); (b) Variation of K, Rb and K/Rb ratio across the granite.

north of the granite proper (nos. 34. 35) shows ratios comparable with those of the western half. It is thought to have resulted from "feldspathization" of the pre-existing gneisses caused by the granite intrusion (Mrs. Nilssen: personal communication) for all gradations between gneiss and granite occur in this area (Barth, 1956, p. 29). The presence of Cs and high Pb and Tl indicated that it is more differentiated than the true granite feldspars, which is in accord with such an origin.

As can be seen from Fig. 3, the two granites can be separated by distinctive K and Rb values.

*The large pegmatites.** Many of the large pegmatites show somewhat greater than average amounts of Rb but several show distinct enrichment of Rb with

* All our samples listed from "large pegmatites" are from pegmatite quarries except for the pegmatite at Varoddbrua (nos. 84 and 85) which is of comparable dimensions with the rest.

respect to K with points falling well to the right of the normal limits of scatter (Fig. 5).

Feldspars from the pegmatites at Kalstad (51) and Tangen, Kragerø (54, 55), Mannekleiv, Iveland (76) and Varoddbrua (85) show mild enrichment. Those showing clear enrichment with Rb contents of more than about 900 p.p.m. are from the pegmatites at Hinnebu (59, 60) and Lauvrak (61, 62) in Øst-Agder, some of the Iveland group (Tuftan, 74, 75; Heia, 77; Knutten, 78), one sample from Varoddbrua (84) and the three from Rømteland (86, 87, 88). The two amazonite

Table 2. Ca, Sr and Ba values in certain feldspars

Sample no.	Rock type	Ca (%)	Sr (p.p.m.)	Ba (%)	Na (%)	K (%)	Rb (p.p.m.)
2	Arendalite (440) Arendal	1·80	500	0·54	2·95	5·37	77
3	Arendalite (441) Hisøy	1·25	160	0·12	4·28	5·77	98
4	Arendalite (442) Langsev	1·40	130	0·27	3·27	5·89	46
5	Gneiss (407) Hisøy	0·66	190	0·32	3·52	7·51	185
21	Augengneiss (422) Ås	0·78	1100	1·25	2·16	9·33	160
40	Fevig granite (414) Moisanden	0·56	425	0·25	2·60	9·09	370
82	Amazonite (429b) Flåt	0·32	150	0·0125	1·26	11·72	1730
83	Pegmatite (421) Ås	0·43	350	0·068	1·97	10·13	280

samples (69, 82) show marked enrichment. Some correlation exists with Cs content in that no pegmatite feldspar enriched in Rb has less than 10 p.p.m. Cs.

Anomalous K/Rb *ratios*

Enrichment of Rb i.e. anomalously low K/Rb ratios has long been known from small volume residuals of magmatic origin (Ahrens, *et al.* 1952; Goldschmidt, 1954, p. 164) and has been reported in highly differentiated igneous granites (Taylor *et al.* 1956). Such enrichment is usually explained by the classical geochemical theory of radius difference, the 10 per cent difference in radius between K^+ (1·33 Å) and Rb^+ (1.47 Å) becoming effective under extreme conditions. Many slight trends of this sort are probably concealed by lack of really precise analytical data but no undoubted trends have been reported except in the Fevig granite reported above. Suites of rocks from the strongly differentiated Skaergaard intrusion do not show significantly different K/Rb ratios (Ahrens *et al.*, 1952; Wager and Taylor, unpublished data).

No clear instances of relative impoverishment in Rb have been reported except some early results by Tolmachev and Filipov (1934) who report high K/Rb ratios in nephelines. Goldschmidt comments on these results and points out that "potassium is not allowed unrestricted entry into the crystal lattice of nepheline and the entrance of the larger ion of rubidium will be still more limited" (Goldschmidt, 1954, p. 167).

During the course of several hundred determinations of the K/Rb ratio at Oxford, a few samples have shown undoubtedly high ratios indicating impoverishment in Rb. These samples have been from rocks occurring with charnockites (HEIER, unpublished data) and syenites (AHRENS, personal communication; UPTON, personal communication). The feldspars discussed in this paper which show anomalous ratios are from arendalite (=Charnockite) (2, 3, 4) (BUGGE, 1940) and an augengneiss (21).

Table 3. Calculated values of theoretical feldspar components

Sample type	Rock type	$KAlSi_3O_8$	$NaAlSi_3O_8$	$CaAl_2Si_2O_8$	$SrAl_2Si_2O_8$	$BaAl_2Si_2O_8$	$RbAlSi_3O_8$	Σ
2	Arendalite (440)	38·4	33·5	12·5	0·19	1·5	0·029	86·1
3	Arendalite (441)	41·1	48·9	8·7	0·06	0·31	0·037	99·1
4	Arendalite (442)	42·1	37·2	9·7	0·05	0·73	0·017	89·8
5	Gneiss (407)	53·6	40·3	4·6	0·07	0·87	0·070	99·5
21	Augengneiss (422)	66·5	24·7	5·4	0·41	3·4	0·061	100·5
40	Fevig granite (414)	64·8	29·7	3·9	0·16	0·67	0·14	99·4
82	Amazonite (429b)	84·0	14·4	2·2	0·06	0·03	0·66	101·4
83	Pegmatite (421)	72·2	22·5	3·0	0·13	0·19	0·11	98·1

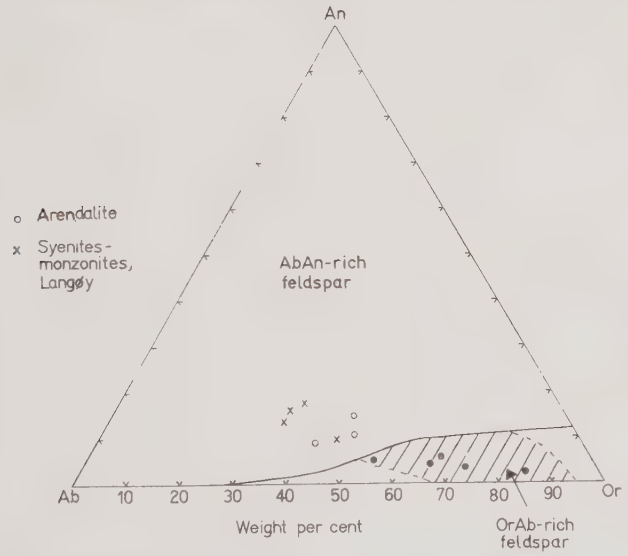

Fig. 7. Feldspar compositions (see Table 3) plotted on the projection of the quaternary system $NaAlSi_3O_8$(Ab)—$KAlSi_3O_8$(Or)—$CaAl_2Si_2O_8$(An)—H_2O at 5000 bars H_2O pressure (YODER *et al.*, 1957). The shaded area indicates the compositional limits of the eighty feldspars not included in Table 3. The solid line separates the AbAn-rich field (above the line) from the OrAb-rich field.

In order to establish the complete feldspar composition we have analysed a selected group for Ca, Sr and Ba. The results are shown in Table 2. The samples were selected to cover a wide range of K/Rb ratios and include the four samples (2, 3, 4, 21) with anomalously low Rb content, two with Rb less than the average (5, 83), one with close to the average (40) and one enriched in Rb (82). The most striking result is that all the feldspars impoverished in Rb contain large amounts (>1 per cent) of Ca. In fact a rough inverse correlation exists between Ca and Rb.

Sr shows no correlation with Rb impoverishment but Ba tends to be high in those samples low in Rb.

The calculated values for the theoretical end member components are given in Table 3. Considering that several independent methods of analysis are involved the summations must be considered satisfactory except for samples 2 and 4. Semi-quantitative spectrographic analysis indicates that SiO_2 is present in excess of the amounts required to form the feldspar components Or, Ab and An, and thus it seems most probable that the samples contain admixed quartz. (The rocks contain up to 20 per cent modal quartz (Bugge, 1940)). Uncrushed material is no longer available since the samples were separated elsewhere. In any event, the significance of the abnormal K/Rb ratio is not affected.

Fig. 7 shows a plot of feldspar composition on a projection of the quaternary system $NaAlSi_3O_8$(Ab)—$KAlSi_3O_8$(Or)—$CaAl_2Si_2O_8$(An)—H_2O at 5000 bars H_2O pressure. This diagram is from Yoder *et al.* (1957). Analyses are plotted as weight per cent Or, Ab and An. The cotectic curve separating the fields from which OrAb-rich feldspars and AbAn-rich feldspars crystallize out are indicated. The pressure is probably somewhat higher than that usually assigned to the ganulite facies but is close enough to make the diagram usable. In the OrAb-rich field the shaded area indicates the composition limits of our samples exclusive of those in Table 2. The limits are approximate since An is taken as 100–(Or + Ab), thus including Ba, etc. True An values will be lower. Even so, with one exception (43) (this sample contains some admixed plagioclase) all fell within the OrAb-rich field, as do all samples 5, 21, 40, 82 and 83 from Table 2 (full circles). The feldspars from the arendalites (2, 3 and 4), however, fall within the AbAn-rich field (open circles in Fig. 7). Also plotted are feldspar compositions (crosses) from syenites monzonites occurring with charnockites at Langøy, Lofoten-Vesterålen Islands. These feldspars are also impoverished in rubidium (Heier, unpublished data). Sample 21 (feldspar from augengneiss), which is impoverished in Rb (although not as much as the arendalites) falls in the OrAb-rich field, but contains a large amount (1·25 per cent) of Ba. This is over twice as much as any other sample.

Our results indicate that rubidium is preferentially excluded from alkali feldspars, which, although containing substantial amounts of potassium, have a composition which places them in the AbAn-rich field of Fig. 7.

All the feldspars were found to be unmixed, usually as common perthites, but as mesoperthites (Michot, 1951) in those from the arendalites and related feldspars in the AbAn-rich field of Fig. 7.

These AbAn-rich feldspars are structurally unfavourable to potassium and rubidium containing a restricted number of sites able to accomodate large ions. In such cases the 10 per cent difference in ionic radius between K and Rb may become critical. The smaller K ion may be more readily accepted.

However, a purely structural explanation for the exclusion of Rb cannot be completely valid, since plagioclase has normal K/Rb ratios. (This is indicated by the normal ratios of basic and intermediate igneous rocks, and also of the few analyses of plagioclase feldspars available.)

The additional factor seems to be the concentration of potassium in the system from which the feldspars are crystallizing. In the cases where rubidium is depleted,

the system has a composition very close to the point where an independent OrAb-rich feldspar will appear as the stable phase. Potassium is thus very abundant and may be thought as "forcing" itself into the crystal lattice, which has a restricted number of sites for large ions. Rb, present in much lower amounts and at a size disadvantage in this competition, will be excluded in favour of potassium in this somewhat unusual case.

If much barium (Ba^{2+} 1·3 Å) enters the feldspar lattice, as in samples 21, the classical capture principle may operate to exclude Rb rather than K.

It seems worthwhile pointing out that the AbAn-rich feldspars impoverished in Rb lie close to the maximum of the subsolidus curve for alkali feldspars separating the one and two feldspar regions, indicating maximum instability for a single feldspar phase. Our hypothesis for the impoverishment of Rb implies that the original feldspar was a homogeneous phase and that the present mesoperthitic nature is due to unmixing and not to replacement at lower temperatures.

Caesium. Cs was detected in several of the feldspars from the granites from the Telemark formation, and in small amounts from two samples (16, 17) from the gneisses. It seems to be potentially the best element which could be used to distinguish the augengneiss feldspars (without detectable Cs) from the anatexe granite feldspars, which may contain amounts (up to 38 p.p.m.) well above the crustal average. Before it can be satisfactorily used, however, the detection limits need to be extended to about 0·1 p.p.m.

Cs was detected in the feldspar (no. 35) from the appendix to the Herefoss granite, but not in the granite feldspars, nor in those from the Fevig granite, and in only one small pegmatite associated with the Oddersjå anatexe granite, which tends also to contain Cs.

The element was detected in most of the feldspars from large pegmatites. Cs shows a general, but not complete correlation with Tl and Rb, but not with lead. The high concentration (700 p.p.m.) in the amazonite feldspar (no. 82) and in the K-feldspar from Varoddbrua (no. 84; 100 p.p.m.) are noteworthy. These samples also contain the greatest amounts of Rb.

Lead. Pb^{2+} (1·20 Å) is frequently found in feldspars. Wedepohl (1956) gives an average of 25 p.p.m. for normal feldspars and 100 p.p.m. for pegmatite feldspars. Our samples range from those in which Pb was not detected (<2 p.p.m.) to a maximum of 160 p.p.m. in a pegmatite feldspar (no. 80).

Lead was detected in only one of the arendalite feldspars at 5·4 p.p.m. and is probably excluded from the lattice for similar reasons as Rb. The Telemark basement granite and gneiss feldspars range from 6·2 to 38 p.p.m. Pb averaging 18 p.p.m. (the crustal average is 15 p.p.m. (Wedepohl, 1956)). The Herefoss granite feldspars are low in Pb, averaging 9 p.p.m. except for no. 35 from the appendix, which has 28 p.p.m, as well as high Cs and Tl. This again suggests that this feldspar is more fractionated than the true granite feldspars. The Fevig granite shows higher amounts (average 26 p.p.m.) than the Herefoss granite. The small pegmatites are average but the large pegmatites show interesting differences.

Many (nos. 59, 60, 61, 62, 72–83, 86–88) show typical high amounts (average 71 p.p.m.). Those associated with the Herefoss granite (nos. 63–71) average 27 p.p.m. (range 13–41 p.p.m.) but those from Kragerø and Arendal (nos. 50–58) and

Varoddbrua (84, 85) have either no detectable lead or very low amounts compared with the other feldspars.

Thallium. Tl^+ (1·47 Å) is the same size as Rb^+, and the two elements show close geochemical coherence. In Fig. 8 Rb is plotted vs. Tl. This diagram is due originally to Ahrens (1948) and on it are indicated his average Rb/Tl line and the limits of scatter (dashed lines) of his plotted points. All our results except three (samples nos. 78, 80 and 82 from large pegmatites) fall within the limits of Ahrens' data.

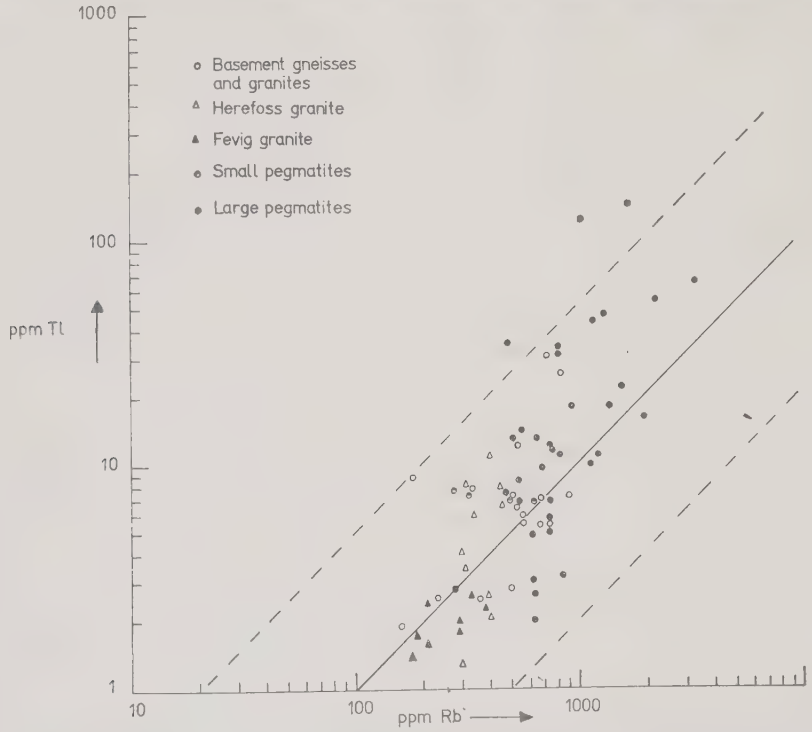

Fig. 8. Relationship between rubidium and thallium for all samples. The solid line is the average slope from Ahrens (1948) Rb—Tl plot. Dashed lines indicate limits of scatter of Ahrens (1948) data.

Several points are apparent from the graph. The Fevig granite feldspars are rather uniformly low in Tl, averaging 2·0 p.p.m., and are distinct from the Herefoss granite feldspars which have a wider spread and average 4·5 p.p.m. The small pegmatites have close to average Rb/Tl ratios and are uniform in Tl content. The gneisses show variable amounts and two of the feldspars from anatectic granites have 25 and 30 p.p.m.

The large pegmatites show a general trend toward relative enrichment in Tl except for samples from Ås (82), Lindvikskollen (52), Tangen (54), Gloserhei (56) and Eretveit (73). None of these except Tangen show Rb enrichment. The pegmatites associated with the Herefoss granite (63–71) have much the same range as the granite itself. The feldspars which show Rb enrichment all contain significant amounts of Tl, averaging 50 p.p.m. but ranging from 10 to 140 p.p.m.

Shaw (1957) in a survey of the geochemistry of Tl notes that Tl follows Rb

rather than K and our results confirm this. However, our results also show that Tl tends to be relatively more enriched in the late differentiates compared with Rb (Fig. 8). Shaw (1952) reports three analyses of feldspars from pegmatites ranging from 21 to 84 p.p.m. Ahrens (1948) found values for Tl in 55 "early pegmatitic" feldspars from 0·4 to 20 p.p.m., for three "hydrothermal pegmatitic" feldspars 48 to 180 p.p.m. and for 16 "late pegmatite" feldspars from 6·0 to 77 p.p.m. Tl. Three granitic feldspars averaged 0·8 p.p.m. Shaw (1952) found total Tl in granites to range from 1·4 to 6·4 p.p.m. Presumably feldspars from these rocks would contain Tl contents of the same order of magnitude. Ishimori and Takashima (1955) found

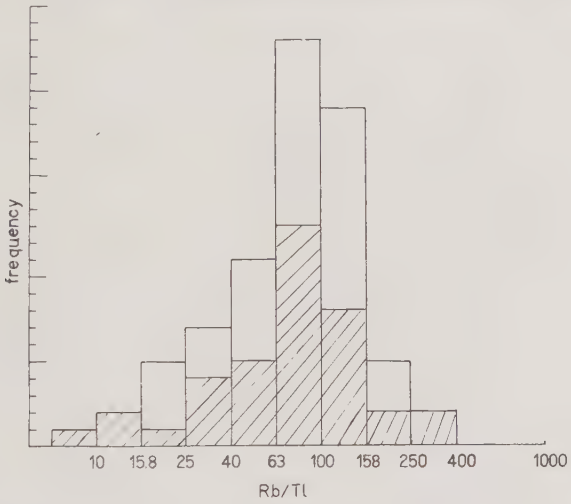

Fig. 9. Histogram of the log (Rb/Tl) ratios for feldspars from large pegmatites (shaded areas) and remaining samples (clear areas).

that three pre-Cambrian gneisses ranged from 0·6 to 0·19 p.p.m. Three composite shale samples ranged from 2·2 to 2·4 p.p.m.

Tauson and Buzayev (1957) found that K-feldspars from the Susamyr batholith contained from 1·7 to 2·4 p.p.m. Tl. They found Tl to be concentrated in the late differentiates, and more abundant in biotite than feldspar.

Of the basement rocks, the feldspars from the gneisses show somewhat erratic values occasionally reaching figures as high as 12 p.p.m., but including samples where Tl was not detected (<1 p.p.m.).

Our results are based on Tl standards kindly supplied by Dr. Denis Shaw, and should thus be directly comparable with his results.

The arithmetic mean of the Rb/Tl ratios is 92 and the geometric mean is 66. If a histogram is prepared of the ratios using a linear scale, extreme positive skewness is shown. However, if these are plotted using a logarithmic scale a symmetrical curve is obtained (Fig. 9). The distribution thus approaches lognormality and am/gm calculates at 1·39, rather close to the value of 1·36 reported by Ahrens (1954b, p. 126) for the Rb/Tl ratio in a large number of potassium minerals. Fig. 9 is more symmetrical than Fig. 5 of Ahrens (1954b, p. 126) which included data from muscovite as well as a number of pegmatite feldspars with high Rb/Tl ratios. In our diagram, a power factor of 1·58 is used to give the interval. A slight amount

of negative skew is shown by the frequency diagram. The shaded areas in Fig. 9 indicate the Rb/Tl ratios for the large pegmatites and it can be seen that some extreme low values of the ratio for some large pegmatites are responsible for the skewness.

4. Geological Significance of Results

Basement gneisses and granites

The feldspars from the basement gneisses show several interesting relationships. The crystal chemical significance of the Rb impoverishment in the feldspars from

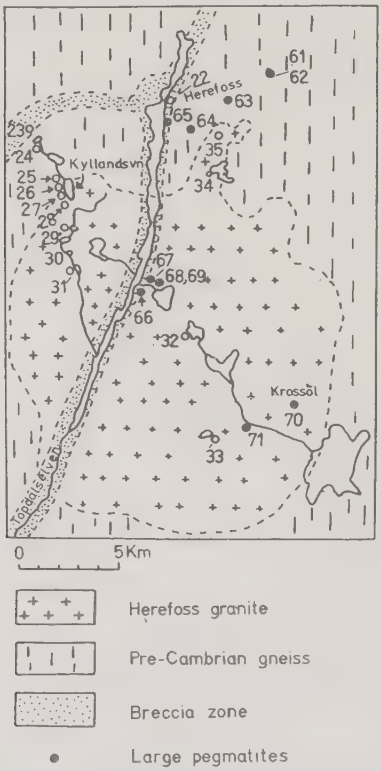

Fig. 10. Geological sketch map of the Herefoss granite showing sample localities (map after Barth, 1948).

the arendalites has been discussed. This may imply depletion of Rb in such rocks but on the other hand is probably only a local impoverishment due to the composition of the feldspar phase. This will occur under other geological conditions and possibly accounts for Rb depletion in syenites (see Goldschmidt, 1954, p. 152). Cs, Pb and Tl are all excluded from the arendalite feldspars (impoverished in Rb) and only Ba seems to be able to enter the lattice with ease.

The feldspars from the Telemark formation come from several distinct rock types: gneisses, augengneisses, granites, grading without sharp contact into the surrounding gneisses. The distinctive feature is this lack of sharp contacts.

The augengneiss feldspars can be distinguished by having no detectable Cs,

generally low Tl and comparatively low Rb (one is anomalously low in Rb). The one augengneiss sample analysed for the alkaline earth elements contains large amounts of Sr and Ba.

The feldspars from the anatectic granites form a different group tending to contain Cs, Tl, and to be higher in Rb. Further work is needed to confirm these trends but it seems possible to separate the feldspars from gneisses, augengneisses and anatectic granites on the basis of trace-element composition.

Diapire (post-orogenic) granites

Feldspars from two of these granites, Herefoss (=Birkeland) and Fevig (= Grimstad) have been analysed. The Fevig granite cuts across the schistosity of the gneisses (Oftedal, 1937) but in the case of the Herefoss granite, "the contacts are either conformable with the gneiss . . . (and) no typical "intrusive" contacts can be seen; or the contacts are transitional as illustrated by the northern offshoots" (Barth, 1956, p. 29).

Samples 23, 24 and 25 are from gneiss close to the north-western side of the Herefoss granite contact (Fig. 10) and form part of a traverse across the contact (samples 23–31). The Herefoss granite feldspars are distinct in composition from these of the gneisses, having in general higher Na, lower K, Rb and Pb. They show some uniformity in composition, except for samples 34 and 35 which come from the northern appendix or offshoot. Of these two, only no. 35 shows a notable increase in the amount of Cs, Pb and Tl, indicating perhaps that it is more differentiated. Samples 32 and 33 from the eastern half of the granite, which is separated by a major fault (Figs. 1 and 10) from the western half, have lower K/Rb ratios. The large pegmatites 63–71 seem to be definitely associated with the Herefoss granite. They form a rather uniform group, being distinctly higher in Cs, Pb and Tl than the granite, and rather comparable in composition to no. 35 from the appendix.

The Fevig granite (Fig. 6) which forms a good example of an intrusive granite, though no thermal metamorphic aureole can be seen (Barth, 1956, p. 34), has feldspars quite different in composition from the Herefoss granite. They contain more Na and less K. On the K/Rb plot (Fig. 3) they fall in distinct areas and might be separated on that criterion alone. The Fevig granite contains higher amounts of lead (average: 26 p.p.m.) than the Herefoss which averages 9 p.p.m. Thallium is lower in the Fevig granite, averaging 2·0 p.p.m. (range: 1·4–2·6 p.p.m.) whereas the Herefoss granite feldspars average 4·5 p.p.m. Tl. Perhaps the most interesting feature of the Fevig granite is the regular change in the K/Rb ratio toward the centre (Fig. 6), rubidium increasing relative to potassium as the centre is approached (see section on Rb). The red granite vein in the gneiss close to the granite contact (sample 43) has a K/Rb ratio close to that of the centre of the granite, and is interpreted as being derived from the granite and not from the country rock in much the same way as the feldspars from the northern appendix are related to the Herefoss granite.

The small pegmatites

One of the most interesting features is that the feldspars from the small pegmatites show little difference from the feldspars in the surrounding rocks, and offer

little evidence for an injected or intrusive origin. In Table 4 are given the analytical data for three samples from a well-exposed roadcut in augengneiss at Kristiansand. No. 18 is a feldspar from the augengneiss; no. 46 is from a lenticular pegmatite body 1 m long and 15 cm maximum width; no. 47 is from a conformable pegmatite vein 50 cm wide and extending for about 10 m completely across the outcrop.

Table 4. Comparative data for feldspars from two small pegmatites and enclosing augengneiss

Sample no.	Rock type	Li p.p.m.	Na %	K %	Rb p.p.m.	Cs p.p.m.	Pb p.p.m.	Tl p.p.m.
18	Augengneiss	1·2	1·80	9·65	340	—	14	7·9
46	Small pegmatite	0·5	1·21	10·50	330	—	19	7·2
47	Pegmatite vein	—	1·62	10·96	420	—	17	—

Table 5. Average values and ranges in composition for groups of large pegmatites

Group		K/Rb	Rb p.p.m.	Cs p.p.m.	Pb p.p.m.	Tl p.p.m.
I	Average of nos. 50–58 from Kragerø and Arendal.	152	690	3·9	3·3*	9·3
	Observed range	115–195	510–880	0·8–14	n.d.–4·9	2·6–33
II	Average of nos. 63–71 from Herefoss granite (except 69)	178	650	13*	25	8·5*
	Observed range	137–215	480–810	n.d.–22	13–41	n.d.–11
III	Average of nos. 59–62 and 72–88 (except 82, 83).	107	1230	29	66	26
	Observed range	34–202	500–3400	n.d.–100	6–160	2·0–120

* Average of samples in which element was detected.

The samples were taken within a few metres of each other. Apart from the absence of Tl in no. 47, little difference can be seen and no evidence for a different origin appears from this data. The same is true in the case of sample no. 48 from a vein in the Oddersjå anatexe granite which does not differ appreciably from the feldspars from the granite.

The large pegmatites

The origin of these bodies is much disputed (see, for example Jahns, 1955). Whereas the feldspars from the small pegmatites have compositions not very different from country rock feldspars, extremes in composition are shown by those from the large pegmatites. It is possible to establish three distinct groupings of the pegmatites. The first group (I in Table 5) are those from Kragero and Arendal (nos. 50–58). Those pegmatites associated with the Herefoss granite form a second rather distinct group (II) (nos. 63–71) which have analogies in composition to the Herefoss granite, although containing greater amounts of most trace elements. The

third group (III) which comprises the remaining feldspars (excluding the amazonite sample 82 and the pegmatite from Ås, 83) is marked by being enriched in Rb, Cs, Pb or Tl.

Fig. 11 shows a frequency plot of the K/Rb ratios for the three groups. The power factor employed to give the interval is 1·58. The tendency of the third group to have low K/Rb ratios is apparent. Table 5 gives averages for the various groups,

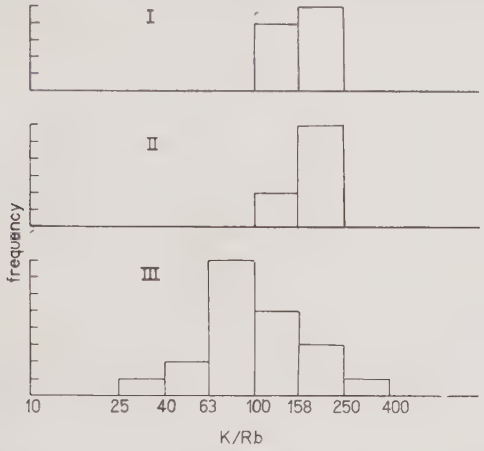

Fig. 11. Histograms of log K/Rb in the three groups of large pegmatites (see Table 5).

together with the ranges in composition. For the three groups, am/gm calculates at 1·02, 1·01 and 1·10 respectively. Ahrens (1954b) found a value of 1·06 for 283 K/Rb ratios. It seems reasonable that group II is derived from the Herefoss granite although the mechanism of formation remains obscure. Group I is similar in composition to the general basement feldspars, except for its anomalously low lead content. It does not seem desirable to invoke regional differences without much clearer evidence. The low lead content of pegmatite feldspars from Kragerø and Gloserhei, Arendal, has been noted by Oftedal (1954).

Table 6

Sample no.	Rock type	Li p.p.m.	Na %	K %	Rb p.p.m.	Cs p.p.m.	Pb p.p.m.	Tl p.p.m.
21	Augengneiss	0·7	2·16	9·33	160	—	19	1·9
83	Large pegmatite	1·0	1·97	10·13	280	—	42	2·8

Within the third group, there are many differences. Thus the samples from the Uranium mine pegmatite at Evje (79 and 80) have normal K/Rb ratios and no detectable Cs but contain large amounts of Pb and Tl. Samples 84 and 85 from Varoddbrua are low in Pb (6 and 7 p.p.m.) but contain much Rb and Cs.

The question of the origin of the large pegmatites will be discussed in our next paper when the Sr and Ba figures will be available. The present conclusion is that it is possible to group the large pegmatite feldspars into different compositional groups on the basis of the distribution of Rb, Cs, Pb and Tl. Detailed work is

Table 7. Sample localities

No.	Locality
1	Søndeled nr. Risør (444)
2	Amtmannssvingen, highway 40, nr. Arendal (440)
3	Hisøy, nr. Arendal (441)
4	Langsev, nr. Arendal (442)
5	Roadcut, Havsøysund, Hisøy, nr. Arendal (407)
6	Roadcut on N side of Tinnsjøen (446)
7	Sandå (445)
8	Glattetrevn., (K. 1)
9	Varden, Skråstadhgd. (K. 8)
10	Sødal (K. 10)
11	Path from Urdalen (K. 11)
12	Oddersjå (K, 12)
13	Erland (K. 14)
14	Ljosvn. (K. 15)
15	Holskogen (K. 7)
16	Spangereid (K. 23)
17	Røyrås (K. 13)
18	Roadcut, Oddernes, 400 m S of bridge to Kristiansand (431)
19	Feda (K. 4)
20	Hille (K. 3)
21	Ås, 500 m down road from pegmatite (422)
22	Breccia junction, Herefoss (H. x)
23	Railroad crossing at Fidjetun 3·5 km NNW of Kyllandsvn. (H. 71)
24	N end of Fidjetjn. (H. 63)
25	N of Kyllandsvn., 600 m NNW of granite (H. 23)
26	Kyllandsvn., close to contact (H. 24)
27	Kyllandsvn., close to contact (H. 57)
28	S end of Kyllandsvn., 200 m SE of 27 (H. 25)
29	Junction between highway 393 and road to Simenstad (H. 91)
30	N of road junction at Vaeting (H. 27)
31	Close to highway 393, 3 km from contact (H. 51)
32	Rosevn. 2 km E of breccia (H. 72)
33	Road to Grøsle, Årdalen, between Gusdal and Austlandsvn. (H. 84)
34	Hilltop close to Holtebu, 500 m from contact (H. 40)
35	Road to Espestøl, 150 m S of road Herefoss–Mjåvtn., close to contact (H.75)
36	Highway 40, 20 cm S of contact (418)
37	Highway 40, 2 m S of contact, (417)
38	Highway 40, 20 m S of contact (416)
39	Highway 40, Strand Hotel, Fevig (415)
40	Highway 40, S of road junction to Moisanden (414)
41	Highway 40, Vig (413)
42	Highway 40, 100 m N of Bie (412)
43	Highway 40, roadcut 200 m W of Ibsen's house (411)
44	Udal–Lista (K. 16)
45	Arneviken (409)
46	same as no. 18 (432)
47	same as no. 18 (433)
48	Varden, Skråstadhgd. (K. 9)
49	Lakssvelefjeld (K. 24)

Table 7.—(*contd.*)

No.	Locality
50	Kalstad, Kragerø (M. 1a)
51	Kalstad, Kragerø (M. 1b)
52	Lindvikskollen, Kragerø (M. 2a)
53	Lindvikskollen, Kragerø (M. 2b)
54	Tangen, Kragerø (M. 11)
55	Tangen, Kragerø (M. 12)
56	Gloserhei, Froland, nr. Arendal (M. 6)
57	Gloserhei, Froland, nr. Arendal (M. 7)
58	Gloserhei, Froland, nr. Arendal (M. 8)
59	Hinnebu, Aust-Agder (M. 5a)
60	Hinnebu, Aust-Agder (M. 5b)
61	Lauvrak, Aust-Agder (M. 3)
62	Lauvrak, Aust-Agder (M. 4)
63	Øygardstj., 1·5 km N of granite appendix (H. y)
64	Road between Herefoss and Landstveitvn., N of granite contact (H. 87)
65	Close to Herefoss (H. 94)
66	W of Begervn., 1 km SW of Åmli (H. 95)
67	Åmli saw mill (H. 74)
68	Stie (H. 450)
69	Stie (H. 451)
70	Krossøl (H. 82)
71	Valbeland, 3 km. W. of the contact (H. 83)
72	Eretveit, Iveland (M. 13)
73	Eretveit, Iveland (M. 14)
74	Tuftan, Iveland (M. 9)
75	Tuftan, Iveland (M. 10)
76	Mannekleiv, Haverstad, Iveland (424)
77	Heia, Haverstad, Iveland (425)
78	Knutten, Haverstad, Iveland (426)
79	Uranium mine pegmatite, Evje (427)
80	Quarry at road junction to uranium mine, Evje (428)
81	Dump from pegmatite quarry, 300 m S of Flåt Ni mine, Evje (429a)
82	Dump from pegmatite quarry, 300 m S of Flåt Ni mine, Evje (429b)
83	Ås, Evje (421)
84	Roadcut, highway 40, just E of Varoddbrua, nr. Kristiansand (435)
85	Roadcut, highway 40, just E of Varoddbrua, nr. Kristiansand (436)
86	Rømteland 1 (K. 18)
87	Rømteland 2 (K. 19)
88	Rømteland 3 (K. 20)

necessary to investigate to what extent the reported differences in group III are due to zoning in individual pegmatites.

The pegmatite from Ås (83) has a very high K/Rb ratio not matched by any other large pegmatite feldspar. For convenience, its composition is given in Table 6, together with the feldspar from the augengneiss country rock. They can be seen to bear a considerable resemblance to each other, in particular in the K/Rb ratios; and the pegmatite in this respect resembles the small pegmatites. The interesting

possibilities of relationships between the composition of host rock and large pegmatites awaits further investigation.

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References

Ahrens L. H. (1948) The unique association of Tl and Rb in minerals. *J. Geol.* **56,** 578–590.

Ahrens L. H. (1954a) Minor elements in rocks. *Nature, Lond.* **174,** 811–816.

Ahrens L. H. (1954b) The lognormal distribution of the elements (2) *Geochim. et Cosmochim. Acta* **6,** 121–131.

Ahrens L. H., Pinson W. H. and Kearns M. M. (1952) Association of rubidium and potassium and their abundance in common igneous rocks and meteorites. *Geochim. et Cosmochim. Acta* **2,** 229–242.

Barth T. F. W. (1948) The Birkeland granite; a case of petroblastesis. *C. R. Soc. géol. Finlande* **20,** 13–182.

Barth T. F. W. (1956) Studies in gneiss and granite. *Skr. Norske Vidensk Akad.* No. 1, 1–35.

Bugge J. (1940) Geological and petrographical investigations in the Arendal district. *Norsk Geol. Tidsskr.* **20,** 71–112.

Cabell M. J. and Smales A. A. (1957) The determination of rubidium and caesium in rocks, minerals and meteorites by neutron-activation analysis. *Analyst* **82,** (975), 390–406.

Goldschmidt V. M. (1954) *Geochemistry* (Edited by Muir A.). Oxford University Press.

Howie R. A. (1955) The geochemistry of the charnockite series of Madras, India. *Trans. Roy. Soc. Edinb.* **62,** 725–768.

Ishimori T. and Takashima Y. (1955) Thallium content of Japanese igneous rocks. *Mem. Fac. Sci. Kyusyu Univ.* C **2,** 65–74.

Jahns R. H. (1955) The study of pegmatites. *Econ. Geol.* 50th Anniv. Vol., 1025–1130.

Michot P. (1951) Essai sur la géologie de la catazone. *Bull. Acad. Belg. Cl. Sci.* 5e Série, 37.

Oftedal I. (1937) Om Fevig-granitten. *Norsk Geol. Tidsskr.* **17,** 210–213.

Oftedal I. (1954) Some observations on the regional distribution of lead in South Norwegian granitic rocks. *Norsk Geol. Tidsskr.* **33,** 153–161.

Ramberg H. (1956) Pegmatites in West Greenland. *Bull. Geol. Soc. Amer.* **67,** 185–214.

Shaw D. M. (1952) The geochemistry of thallium. *Geochim. et Cosmochim. Acta* **2,** 118–154.

Shaw D. M. (1957) The geochemistry of gallium, indium and thallium—a review. *Physics and Chemistry of the Earth* Vol. II, Chap. 6, pp. 164–211.

Tauson L. V. and Buzayev N. N. (1957) The geochemistry of thallium in granitoids of the Susamyr batholith. *Geokhimya*, No. 7, 600–605.

Tauson L. V. and Stavrov O. D. (1957) On the geochemistry of rubidium in granitoids. *Geokhimiya* No. 8, 699–703.

Taylor S. R., Emeleus C. H. and Exley C. S. (1956) Some anomalous K/Rb ratios in igneous rocks and their petrological significance. *Geochim. et Cosmochim. Acta* **10,** (4), 224–229.

Taylor S. R. and Heier K. S. (1958) Alkali elements in potash feldspars from the pre-Cambrian of southern Norway. *Geochim. et Cosmochim. Acta* **13** (4), 293–302.

Tolmachev Y. M. and Filipov A. N. (1934) Presence of rubidium, beryllium, gallium and strontium in nephelites. *Dokl. Akad. Nauk SSSR* **3,** 366–368.

Wedepohl K. H. (1956) Untersuchungen zur Geochemie des Bleis. *Geochim. et Cosmochim. Acta* **10,** 69–148.

Yoder H. S., Stewart D. B. and Smith J. R. (1957) Ternary feldspars. *Yearb. Carneg. Instn.* **56,** 207–214.

Geochimica et Cosmochimica Acta, 1959, Vol. 15, pp. 305 to 329. Pergamon Press Ltd. Printed in Northern Ireland

Adsorption aus sehr verdünnten Kupferlösungen an reinen Tonmineralen

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Abstract—The adsorption of copper by various clay minerals, and also by quartz and calcite, was studied experimentally at different pH-values and concentrations. The clay minerals used were grain size fractions with an equivalent diameter < 2 or $< 0{\cdot}6\ \mu$ of two kaolinites, one fireclay type kaolinite, two illites and two montmorillonites. The surface properties of these samples were determined in part in electron micrographs and by the glycol-retention method.

Copper is adsorbed by clay minerals and by quartz according to the Freundlich adsorption isotherm whereas in the case of calcite a chemical reaction takes place. The adsorption capacity of the clay minerals is increased by raising the pH as well as the copper concentration. The influence of concentration and pH-value is most pronounced with the kaolinites, there is only a small influence with the montmorillonites. The adsorption capacity related to 100 g of clay increases in the following order: kaolinite, fireclay type kaolinite, illite, montmorillonite. However, the adsorption capacity related to 100 m^2 surface of kaolinite and fireclay type kaolinite are of the same order of magnitude, the adsorption capacity per surface unit for illite and montmorillonite can be considerably smaller under certain conditions.

The significance of such adsorption for geochemical processes is briefly discussed.

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Einleitung

Seit langem beschäftigt man sich mit der Frage der Bildungsweise verschiedener sedimentärer Lagerstätten und suchte nach Erklärungen für die Schwermetallgehalte in Sedimenten. Schon im Jahre 1903 machte Kohler (1903) darauf aufmerksam, dass für die Lösung dieser Fragen der Adsorptionsvorgang von grosser Bedeutung sein kann. Es sind seitdem eine ganze Reihe von Untersuchungen auf diesem Gebiet durchgeführt worden. Man studierte die verschiedensten Adsorbentien, wie Tonminerale, organische Substanz, kolloidales $Fe(OH)_3$ und andere anorganische Kolloide in ihrer Wirkungsweise auf die verschiedenen

Metallionen. Eine zusammenfassende Untersuchung und Darstellung dieser Probleme gibt Krauskopf (1956) in seiner Arbeit.

Auch das spezielle Thema der Kupfer adsorption an Tonmineralen ist schon frühzeitig bearbeitet worden. Correns (1924) untersuchte das System Kupfer–Kaolin und zwar in stark verdünnten Kupfer lösungen. Da in den natürlichen Gewässern der Kupfer gehalt auch sehr niedrig ist (1-15 γCu/l.), kann man aus solchen Versuchen am ehesten Rückschlüsse auf das Verhalten des Kupfers bei geochemischen Prozessen ziehen. Die hier vorliegende Arbeit ist nun insofern eine Erweiterung der Arbeit von Correns als neben Kaolinit auch andere reine Tonminerale zur Untersuchung herangezogen und die Messungen bei verschiedenen pH–Werten durchgeführt wurden.

Untersuchungsmaterial und angewendete Methoden

Angaben über die verwendeten Proben und ihre Vorbehandlung

Als Ausgangsmaterial für die Adsorptionsversuche wurden verschiedene Tonminerale, sowie zwei unterschiedlich behandelte Quarzproben und eine Calcitprobe verwendet.

Die Tonminerale wurden aus Rohtonen abgetrennt, von denen bereits bekannt war, dass sie hauptsächlich nur ein einziges Tonmineral enthalten.

Kaolin Westerwald	KW
Kaolin Zettlitz	KZ
Glashafenton von Gross-Almerode	FC
Illitton von Fithian/Illinois	H-35
Illitton von Morris/Illinois	H-36
Montmorillonit von Polkville/Mississippi	H-19
Montmorillonit von Upton/Wyoming	H-25

Da bekannt ist, dass die reinen Tonminerale in den feinsten Fraktionen am stärksten angereichert sind, wurden aus den Gesamttonen die Fraktionen mit einem Aquivalentdurchmesser von $<0{,}6$ und/oder $<2\ \mu$ durch wiederholte Sedimentation im Atterbergzylinder abgetrennt. Als Dispersionsmittel wurde 0,01 n NH_4OH –Lösung benutzt, die mit doppeltdestilliertem Wasser angesetzt war. Zur Prüfung auf Reinheit wurde ein Teil der feinen Fraktion (<0.6 und/oder $<2\ \mu$) als Texturpräparat z.T. nach verschiedener Vorbehandlung röntgenographisch auf einem selbstregistrierenden Beugungsgoniometer und in einer Kamera nach Jasmund (1950) untersucht.

Dabei ergab sich folgendes: Der Kaolin Westerwald stammt aus einer Bohrung bei Langendernbach, Kreis Limburg/Lahn. Die Fraktionen $<0{,}6$ und $<2{,}0\ \mu$ (KW 0,6 und KW 2) bestehen aus Kaolinit, der gut geordnet ist. Verunreinigungen liessen sich nicht feststellen.

Kaolin Zettlitz (Fraktion $<2\ \mu$, KZ) ist ein Kaolinit, der etwas Illit als Nebengemengteil enthält.

Der Glashafenton Lengemannschacht von Gross-Almerode (Fraktion $<0{,}6\ \mu$, FC) wurde bereits von Lippmann (1952) untersucht, der für die Fraktionen $<0.6\ \mu$ als Hauptbestandteil Fireclay-Mineral (ungeordneter Kaolin) angibt und daneben

<5% Quarz und ≪10% Illit. Die hier untersuchte Probe zeigte die gleichen Röntgendiagramme.

Die folgenden Proben sind amerikanische Standardproben nach der Nomenklatur der Reference Clay Minerals.

Der Illitton von Fithian/Illinois (Fraktion <2 μ, H-35) enthält neben Bereichen nicht quellfähiger Glimmerschichten auch solche, in denen bis zu etwa 15% der Glimmerschichten in unregelmässiger Wechsellagerung durch quellfähige Schichten (Montmorin-Schichten) ersetzt sein können. Spuren von Quarz und Kaolinit lassen sich nachweisen.

Der Illitton von Morris/Illinois (Fraktion <2 μ, H-36) ist ähnlich gebaut wie der Illitton von Fithian/Illinois. Auch hier befinden sich neben den nicht quellfähigen Glimmerschichten Bereiche, in denen eine unregelmässige Wechsellagerung mit quellfähigen Schichten (bis zu 20%) auftritt. Quarz und Kaolinit sind als Nebengemengteil vorhanden.

Montmorillonit von Polkville/Mississippi (Fraktion <2 μ, H-19) ist in der Literatur bekannt als ein Montmorillonit, der hauptsächlich Ca als austauschbares Kation enthält. Dies wird durch die Lage des Basisreflexes bei 15 Å im lufttrockenen Zustand bestätigt.

Für den Montmorillonit von Upton/Wyoming (Fraktion <2 μ, H-25) wird vor allem Na als austauschbares Kation angegeben. Dies wird durch die Lage des Basisreflexes bei 12,2 Å im lufttrockenen Zustand bestätigt.

Bei beiden Montmorilloniten verschieben sich die Basisreflexe nach Sättigung mit Äthylenglykoldampf nach 17 Å. Dies zeigt, dass sie vollständig aus quellfähigen Schichten aufgebaut sind.

Die Quarzproben wurden vor dem Schlämmen in der Kugelmühle etwa 6 Std trocken gemahlen. Die eine Quarzprobe (Fraktion <2 μ, Q 1) ist ein feingemahlener Dörentruper Quarzsand. Die feine Fraktion wurde durch wiederholte Sedimentation im Atterbergzylinder mit Methanol abgetrennt. Die andere Quarzprobe (Fraktion <2 μ, Q 2) besteht aus feingemahlenem glasklaren Bergkristall ohne Fundortangabe. Hier wurde die feine Fraktion mit NH_4OH-haltigem Wasser abgetrennt. Die Röntgenaufnahmen beider Proben zeigen nur die Quarzlinien.

Für Calcit wurde das Präparat von Merck Nr. 2067, Calciumkarbonat gefällt p.a., verwendet. Die Röntgendiagramme zeigen nur die Calcitlinien, Aragonit ist nicht nachweisbar.

Elektronenoptische Untersuchungen

Bei der Sedimentation im Atterbergzylinder werden die Teilchen auf Grund ihrer Sinkgeschwindigkeit abgetrennt. Es können dabei Teilchen verschiedener Gestalt in eine Fraktion gelangen. Die Angabe "Fraktion <2 μ" gibt also keine genaue Auskunft weder über die Korngrössenverteilung innerhalb dieser Fraktion, noch über die morphologische Ausbildung der Teilchen. Sie erlaubt deshalb auch keine Aussage über ihre Oberflächenbeschaffenheit. Für eine Auswertung der Adsorptionsversuche ist es jedoch wichtig, Angaben über das Verhältnis Oberfläche: Seitenfläche zu haben. Die elektronenoptischen Aufnahmen bieten eine Möglichkeit in dieser Richtung.

Sie wurden folgendermassen ausgeführt: Die auf Lochblenden aufsedimentierten Teilchen wurden unter einem Winkel von 30° einseitig mit Au-Pd bedampft. Durch dieses Schrägbedampfen wird nicht nur ein schärferer Kontrast zwischen Tonteilchen und Untergrund geschaffen, sondern es ergibt sich auch die Möglichkeit, die Dicke der Blättchen und Aggregate zu messen und damit auch etwas über die Seitenflächen der Blättchen aussagen zu können.

Tabelle 1. Korngrössenverteilung in den feinen Fraktionen, Äquivalentdurchmesser (μ)

Probe	2000–1120	1120–630	630–350	350–200	200–112	112–63	63–35
KZ	14	102	493	304	120	26	
KW 0,6		61	166	463	411	109	15
FC		8	21	120	515	575	245

Der Kaolinit Zettlitz zeigt meist sechseckige Blättchen, die in einer Richtung etwas länger sind und eine Dicke von durchschnittlich $\sim$10 μ haben.

Beim Kaolinit Westerwald ist dagegen die sechseckige Ausbildung der Blättchen nicht so deutlich sichtbar. Hier sind die Schichtpakete bis zu 150 μ dick, während die einzelnen Blättchen im Durchschnitt kleiner sind als beim Kaolinit Zettlitz. An sehr dünnen Teilchen lässt sich auch hier die für Kaolinite charakteristische Form erkennen.

Das Fireclay-Mineral von Gross-Almerode besteht ebenfalls aus sechseckigen Blättchen. Doch sind diese im Gegensatz zu den vorher beschriebenen Proben sehr dünn und klein. Das Korngrössenmaximum liegt hier bei noch kleineren Durchmessern.

Die Aufnahmen der Illite können leider nicht ausgewertet werden. Diese Proben zeigen keine gute idiomorphe Ausbildung der Blättchen. Es lässt sich nur erkennen, dass sehr viel feines Material vorhanden sein muss.

Für den Montmorillonit gilt dasselbe. Es ist auch hier unmöglich, vernünftige Aussagen über die Korngrössenverteilung zu machen, wie aus den in der Literatur veröffentlichten Bildern zu ersehen ist. Da aber beim Montmorillonit nach Dyal und Hendricks (1950) die äussere Oberfläche nur etwa 5% der gesamten Oberfläche ausmacht und die Adsorption sich hauptsächlich in den Zwischenschichten abspielt, würden sich durch diese Methode für die Montmorillonite sowieso keine wesentlichen Hinweise ergeben.

Auch die Quarzproben wurden elektronenoptisch untersucht. Sie zeigen entsprechend ihrer Vorbehandlung in der Kugelmühle ganz unregelmässig zerbrochene und zersplitterte Körner verschiedenster Grösse. Aus den Aufnahmen konnten keine Anhaltspunkte für die Auswertung der Adsorptionsversuche gewonnen werden. Vom Calcit wurden keine Aufnahmen gemacht.

Bestimmung der Oberfläche durch Adsorption von Äthylenglykol

Da das elektronenoptische Verfahren nur über die Oberflächenbeschaffenheit der Kaolinminerale einige Aufschlüsse gibt, wurde versucht, vergleichbare Werte

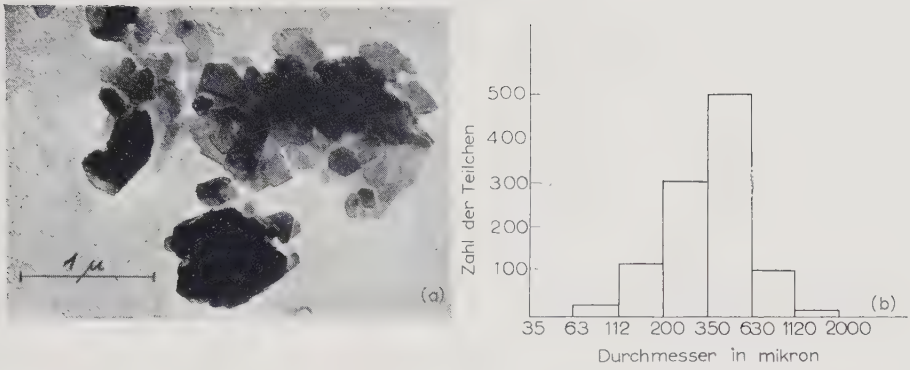


Abb. 1. Kaolinit Zettlitz, KZ, elektronenoptische Aufnahme und Korngrössenverteilung.

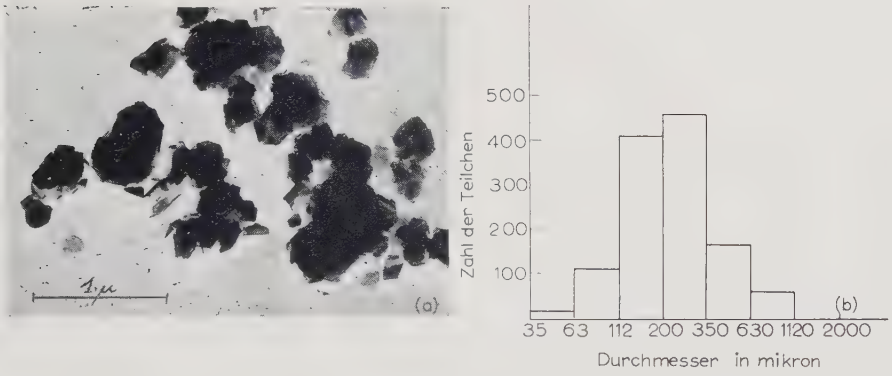


Abb. 2. Kaolinit Westerwald, KW 0,6, elektronenoptische Aufnahme und Korngrössenverteilung.

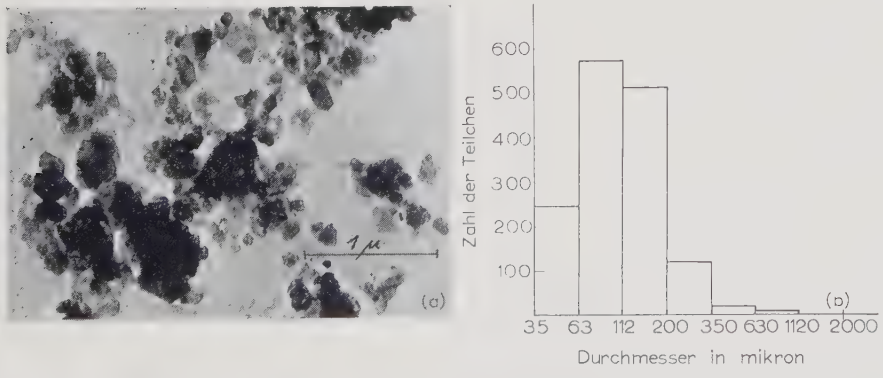


Abb. 3. Fireclay-Mineral, FC, elektronenoptische Aufnahme und Korngrössenverteilung.

für die Oberflächen auch der anderen Proben nach der Äthylenglykolmethode von Dyal und Hendricks (1950) zu erhalten. Bestimmungen der Oberflächen nach der Brunauer Emmett–Teller-Methode (Brunauer, Emmett und Teller, 1938) wurden nicht gemacht, da man mit ihr nur die äussere Oberfläche der Montmorillonite bestimmen kann, nicht aber die innere. Mit der Äthylenglykolmethode bestimmt man dagegen die gesamte einer polaren Flüssigkeit zugängliche Oberfläche. Die auf diese Weise für Glykol gefundenen Werte sollten Anhaltspunkte für das System Ton–Wasser bieten.

Ungefähr 1 g lufttrockener Substanz wird in ein Wägegläschen eingewogen und

Tabelle 2

Probe	Glykol adsorb. (mg/g Ton)	auf m^2 umgerechnet (m^2/g Ton)
Quarz Q 1	3,0	9
Quarz Q 2	2,5	7
KZ	19,6	63
KW 0,6	19,0	61
KW 2	18,0	58
FC	33,4	107
H-35	60,7	196
H-25	238,0	767

über P_2O_5 im Vakuum ($<0{,}1$ mm Hg) bis zur Gewichtskonstanz getrocknet. Anschliessend wird die Probe mit 1 ml doppeltdestilliertem Glykol getränkt und etwa 12 Std in einem Exsiccator über wasserfreiem $CaCl_2$ aufbewahrt. Dann wird das System wieder auf $<0{,}1$ mm Hg evakuiert zum Verdampfen des überschüssigen Äthylenglykols. Die Dauer des Versuches hängt von der Güte des Vakuums ab. Bei den hier vorgenommenen Versuchen betrug die Zeitdauer ungefähr 36 Std.

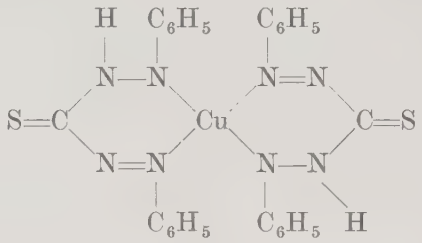
Die Berechnung beruht auf der Annahme, dass das Glykol monomolekulare Schichten auf der Oberfläche bildet. Für die innere Oberfläche glykolgesättigter Montmorillonite kann dies durch die Lage des Basisreflexes bei 17 Å bewiesen werden. Fehler können bei der Bestimmung der äusseren Oberfläche durch die Bildung von doppelten Glykolschichten auftreten. Dies gilt besonders für die Kaolinminerale.

Auf Grund des geringen Adsorptionsvermögens der Kaolinminerale können die Fehler bis zu 25% betragen, für die Montmorillonite, bei denen die innere Oberfläche den grössten Anteil hat, sind die Fehler viel kleiner (bis 6%). (Als Umrechnungsfaktor wird $3{,}1 \cdot 10^{-4}$ g Äthylenglykol/m^2 Oberfläche angegeben.) Die gefundenen Werte zeigt Tabelle 2.

Chemisch-analytische Methoden

Für die Kupfer bestimmung wurde die Dithizon-Kupferdithizonat-Methode angewendet, die sich besonders für die Bestimmung sehr kleiner Kupfer mengen eignet (Fischer, 1937; Brown, 1946; Sandell, 1950). Sie beruht auf der

Tatsache, dass Kupfer-Ionen in saurer Lösung mit Dithizon unter Bildung eines rot-violetten Ketokomplexes reagieren.



Die Bestimmungen wurden folgendermassen ausgeführt:

Reagenzien: 0,001% Dithizonlösung in doppeltdestilliertem CCl_4. (Gewichtsprozent/Volumen)
H_2O, in Jenaer Glasapparatur doppeltdestilliert
0,1% HCl-Lösung, kupfer frei
$CuSO_4 \cdot 5H_2O$ p.a. nach Merck

Die zu bestimmende kupfer haltige Lösung, die nicht mehr als etwa 5 γ Cu/10ml enthalten sollte, wurde mit 1 ml 0,1% HCl-Lösung ungefähr auf einen pH 3 gebracht und nach Zugabe von 10 ml 0,001% Dithizonlösung 6 min geschüttelt. Die CCl_4-Phase zeigt je nach dem Kupfer gehalt eine Mischfarbe zwischen grün und rot-violett. Sie wurde in eine Adsorptionsküvette gefüllt und die Extinktion bei 510 mμ und 625 mμ mit einem Spektralphotometer von Zeiss Typ PMQ II gemessen. Die Eichkurven wurden mit dem gleichen Volumen und Säuregrad aufgenommen, die nachher bei den Versuchen benutzt wurden.

Versuchsausführung

In Schliff-Flaschen aus Jenaer Glas wurden 50 ml einer 0,01% Tonsuspension mit 5 ml einer Lösung bekannten Kupfer gehaltes versetzt. Die Kupfer lösung stellte gleichzeitig (wie unten näher erläutert wird) das gewünschte pH ein. Die Flaschen wurden 60 min bei Zimmertemperatur geschüttelt, anschliessend wurden die Lösungen durch Membranfilter filtriert und im Filtrat der Kupfer gehalt bestimmt. Aus der Differenz der Ausgangskonzentration und der Konzentration im Filtrat ergibt sich die vom Ton adsorbierte Menge. Es wurden Doppelbestimmungen ausgeführt, für die Quarzproben sogar 4-fache, da hier die Adsorption sehr gering ist.

Die grundsätzliche Frage nach der Zeitdauer, die zur Einstellung des Adsorptionsgleichgewichtes jeweils nötig ist, wurde für alle Substanzen geprüft, indem die Abhängigkeit zwischen Zeit und Kupfer konzentration in Lösung über 24 Std verfolgt wurde. Dass die kupfer haltige Lösung zur Einstellung des Gleichgewichtes mit der festen Phase nur eine verhältnismässig kurze Zeit braucht, bestätigt, dass es sich bei den Vorgängen an den Tonmineralen und den Quarzproben wirklich um eine Adsorption handelt und nicht etwa um eine chemische Reaktion, wie dieses beim Calcit zu sein scheint (s.u.). Denn es ist nach Freundlich typisch für die Adsorption, dass sich das Gleichgewicht besonders bei

feinkörnigen Adsorbentien meist nach wenigen Sekunden oder Minuten schon eingestellt hat. Ist die wirksame Oberfläche nicht so leicht zugänglich, so dauert es etwas länger. Dieses stimmt gut mit den Messergebnissen überein. Bis auf geringe Abweichungen beim Montmorillonit zeigte sich für alle Proben, ausser dem Calcit, dass eine Versuchsdauer von 60 min ausreichend ist. Auch BORLAND (1950) fand bei seinen Adsorptionsversuchen mit ^{45}Ca an Tonmineralen eine Zeit von 60 min als genügend.

Die Versuche wurden bei pH-Werten von 5,1, 6,0 und 6,8 durchgeführt, nur für die beiden Quarzproben und die Probe KW 2 wurde bei pH-6, für Calcit nur beim pH-7 gemessen. Die pH-Einstellung der Kupfer lösung erfolgte mit

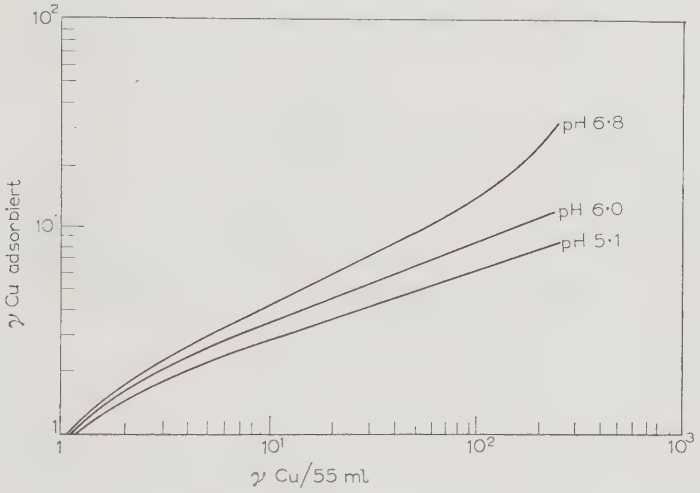


Fig. 1. Kupferadsorption an Glasgeräten und an Membranfiltern.

verdünnter H_2SO_4 bzw. NH_4OH-Lösung. Von der Verwendung von Pufferlösungen wurde abgesehen, um den Adsorptionsmechanismus nicht durch die Gegenwart fremder Ionen zu komplizieren. Sulfat-Ionen sind durch das $CuSO_4$ sowieso in der Lösung enthalten, etwas NH_4OH wird durch die Korngrössentrennung am Ton adsorbiert sein. Das pH wurde in Parallelversuchen kontrolliert, um etwaige Änderungen während des Versuches feststellen zu können, es wurden jedoch keine beobachtet. Es konnte leider nicht bei höheren pH-Werten gemessen werden, da Kupfer dann nicht mehr in Lösung bleibt, sondern als basisches Salz ausfällt. Erst bei noch höheren NH_4-Konzentrationen geht es als $Cu(NH_3)_4$—Komplex wieder in Lösung.

Um die Fehler möglichst klein zu halten, wurden ständig Blindversuche durchgeführt. Es ist wichtig, dass das verwendete doppeltdestillierte Wasser, die Reagentien und alle Gerätschaften stets kupfer frei sind. Ausserdem wurden Versuche ausgeführt, um die Adsorption an den Glasgeräten und den Membranfiltern zu bestimmen.

Es wurden keine Versuche gemacht, um das direkt am Ton adsorbierte Kupfer zu bestimmen. Man kann das Kupfer wieder auswaschen, wenigstens den

grössten Teil, es ist aber fast unmöglich, vorher die gesamte am Ton nicht adsorbierte Kupfer menge aus dem Ton zu entfernen, ohne das Gleichgewicht adsorbiertes Kupfer: gelöstem Kupfer zu stören.

Ergebnisse, allgemeiner Teil

Die Versuchsergebnisse sind in den Tabellen 3–10 und den graphischen Darstellungen 2–9 wiedergegeben. Aus ihnen lässt sich allgemein erkennen:

(1) Die Adsorptionsfähigkeit für Kupfer nimmt von Kaolinit über Fireclay-Mineral und Illit zum Montmorillonit hin zu.

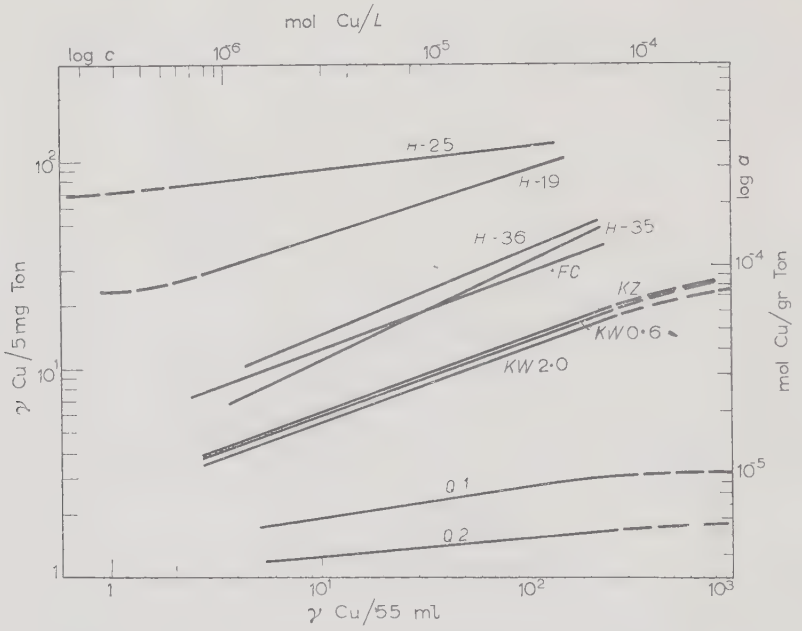


Fig. 2. Adsorptionskurven aller benutzten Tonminerale sowie der beiden Quarzproben beim pH-6.

(2) Mit steigender Kupfer konzentration nimmt die adsorbierte Kupfer menge zu. Bei der graphischen Darstellung im doppeltlogarithmischen Maßstab ergeben sich Geraden.

(3) Mit steigendem pH nimmt die adsorbierte Kupfer menge zu.

Bemerkungen zu diesen Versuchsergebnissen:

Zu (1) dieses Verhalten des Kupfers verläuft parallel mit den für Äthylenglykol bestimmten Adsorptionskapazitäten.

Zu (2) die Tatsache, dass die graphische Darstellung in doppeltlogarithmischen Koordinaten eine Gerade ergibt, zeigt, dass die Adsorption nach der sogenannten Freundlich'schen Isotherme verläuft. Die allgemeine Form der Isotherme ist:

$$\frac{x}{m} = a \cdot c^{\frac{1}{n}}$$

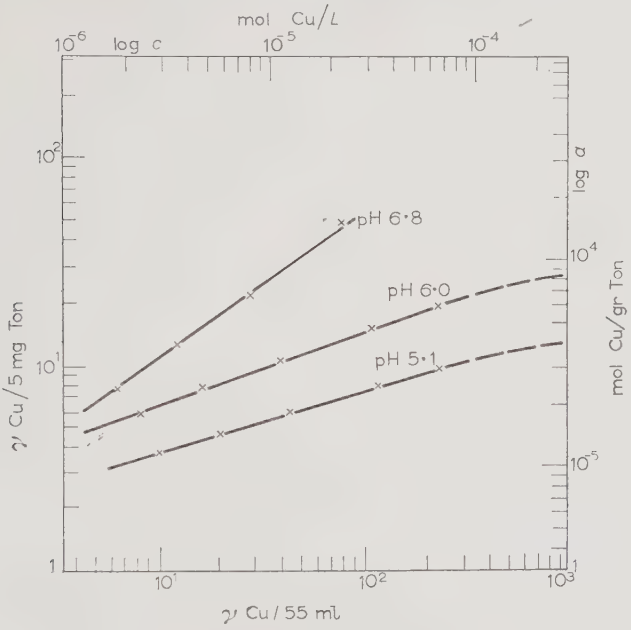


Fig. 3. Adsorptionsversuche an Kaolinit Zettlitz.

Tabelle 3

pH	Anfangskonz. (γ Cu/55 ml)	Endkonz. (γ Cu/55 ml)	ads. Menge (γ Cu/5 mg Ton)	ads. Menge (γ Cu/m²)
5,1	250	240,5	9,5	30,2
	125	117,0	8,0	25,4
	50	44,0	6,0	19,1
	25	20,4	4,6	14,6
	14	10,3	3,7	11,8
6,0	250	231,0	19,0	60,4
	125	110,0	15,0	47,6
	50	39,5	10,5	33,3
	25	17,0	8,0	25,4
	14	8,5	5,5	17,5
6,8	250	—	—	—
	125	77,0	48,0	152,5
	50	29,0	21,0	66,7
	25	12,5	12,5	39,7
	14	6,5	7,5	23,8

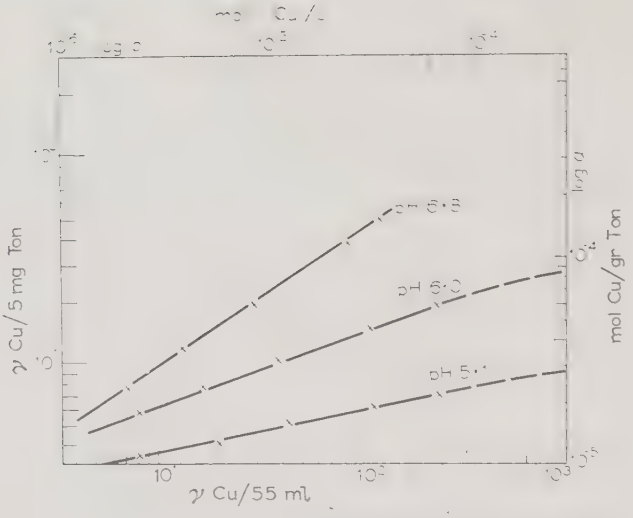


Fig. 4. Adsorptionsversuche an Kaolinit Westerwald KW 0·6.

Tabelle 4

pH	Anfangskonz. (γ Cu/55 ml)	Endkonz. (γ Cu/55 ml)	ads. Menge (γ Cu/5 mg Ton)	ads. Menge (γ Cu/m^2)
5,1	250	243,2	6,8	20,7
	125	118,8	6,2	18,9
	50	44,9	5,1	15,6
	25	21,0	4,0	12,2
	12	8,5	3,5	10,7
6,0	250	231,2	18,8	57,4
	125	110,5	14,5	44,2
	50	39,8	10,2	31,1
	25	17,3	7,7	23,5
	14	8,3	5,7	17,4
6,8	175	125,0	50,0	152,5
	125	87,0	38,0	116,0
	50	31,0	19,0	58,0
	25	13,5	11,5	35,1
	14	6,5	7,5	22,9

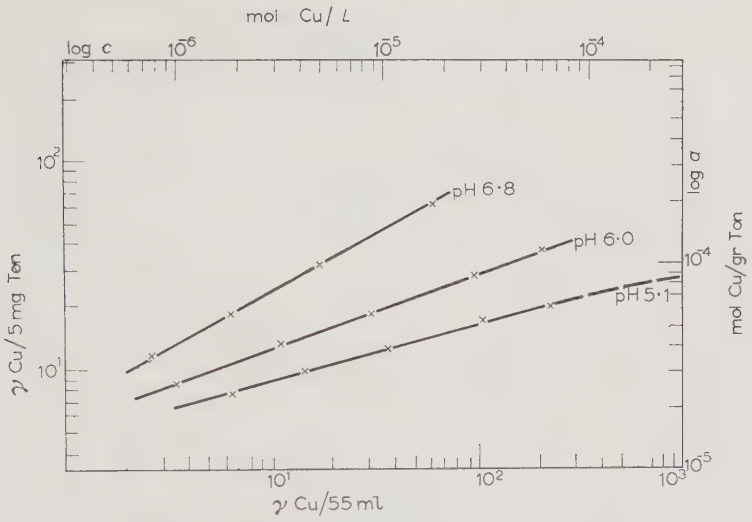


Fig. 5. Adsorptionsversuche an Fireclay-Mineral FC.

Tabelle 5

pH	Anfangskonz. (γ Cu/55 ml)	Endkonz. (γ Cu/55 ml)	ads. Menge (γ Cu/5 mg Ton)	ads. Menge (γ Cu/m²)
5,1	250	230,0	20,0	37,7
	125	107,5	17,5	32,7
	50	37,5	12,5	23,4
	25	15,0	10,0	18,7
	14	6,5	7,5	14,0
6,0	250	212,0	38,0	71,0
	125	97,0	28,0	52,3
	50	31,5	18,5	34,6
	25	11,5	13,5	25,2
	14	5,5	8,5	15,9
6,8	250	—	—	—
	125	62,0	63,0	119,0
	50	18,0	32,0	59,8
	25	6,5	18,5	34,6
	14	2,5	11,5	21,5

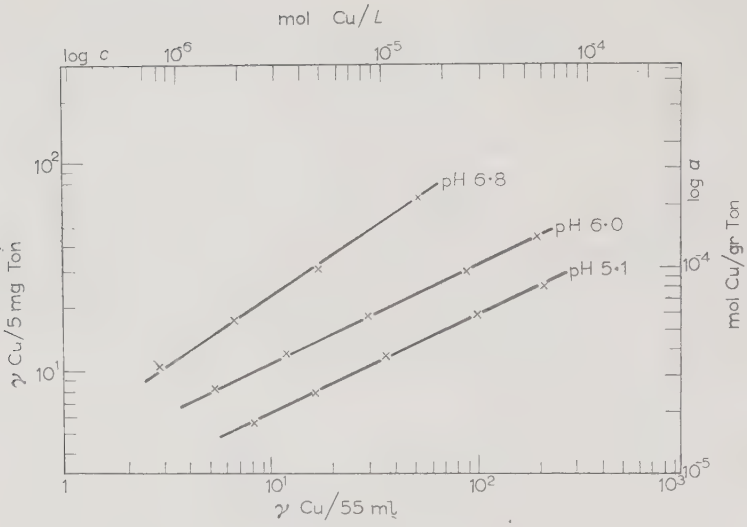


Fig. 6. Adsorptionsversuche an Illit H-35

Tabelle 6

pH	Anfangskonz. (γ Cu/55 ml)	Endkonz. (γ Cu/55 ml)	ads. Menge (γ Cu/5 mg Ton)	ads. Menge (γ Cu/m^2)
5,1	250	224,0	26,0	26,6
	125	105,5	19,5	19,9
	50	38,0	12,0	12,2
	25	17,0	8,0	8,2
	14	8,3	5,7	5,8
6,0	250	205,0	45,0	45,9
	125	94,0	31,0	31,6
	50	31,0	19,0	19,4
	25	12,5	12,5	12,8
	14	5,5	8,5	8,7
6,8	250	—	—	—
	125	54,0	71,0	72,5
	50	18,0	32,0	32,6
	25	7,0	18,0	18,4
	14	3,0	11,0	11,3

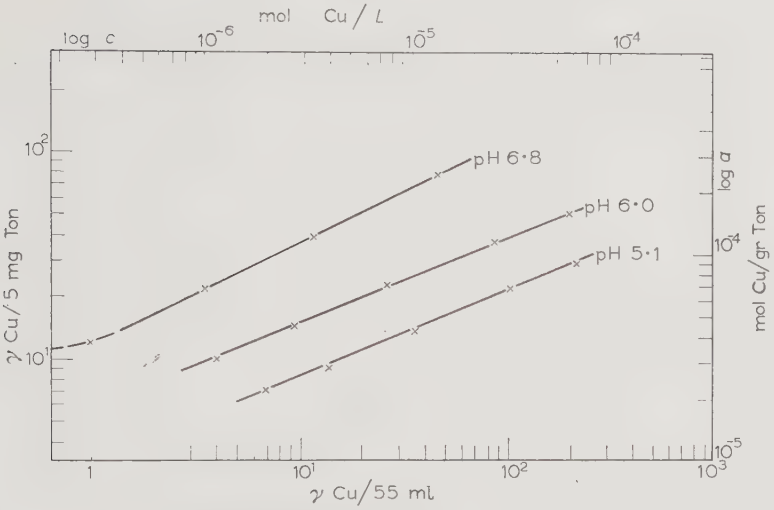


Fig. 7. Adsorptionsversuche an Illit H-36

Tabelle 7

pH	Anfangskonz. (γ Cu/55 ml)	Endkonz. (γ Cu/55 ml)	ads. Menge (γ Cu/5 mg Ton)
5,1	250	221,0	29,0
	125	103,0	22,0
	50	36,0	14,0
	25	14,0	9,0
	14	7,0	7,0
6,0	250	200,0	50,0
	125	88,0	37,0
	50	27,0	23,0
	25	9,5	15,5
	14	4,0	10,0
6,8	250	—	—
	125	47,0	78,0
	50	12,0	38,0
	25	3,5	21,5
	14	—	~ 14,0

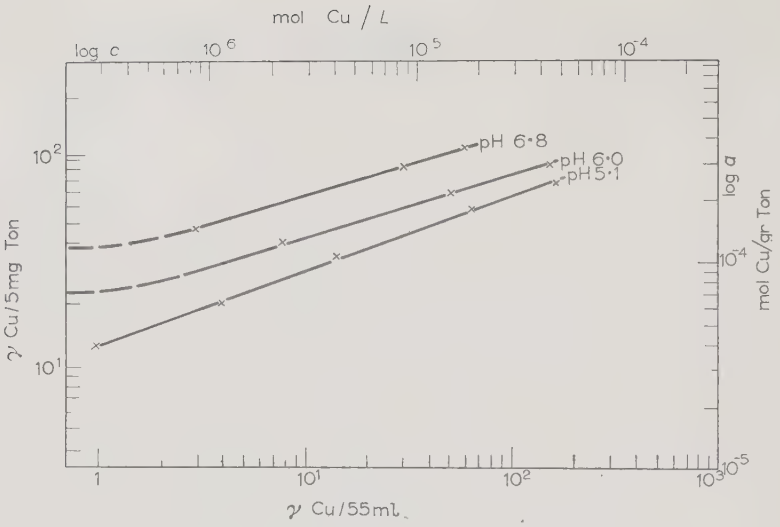


Fig. 8. Adsorptionsversuche an Montmorillonit H-19

Tabelle 8

pH	Anfangskonz. (γ Cu/55 ml)	Endkonz. (γ Cu/55 ml)	ads. Menge (γ Cu/5 mg Ton)
5,1	250	164,0	86,0
	125	65,0	60,0
	50	14,5	35,5
	25	4,0	21,0
	14	1,0	13,0
6,0	250	153,0	97,0
	125	51,0	74,0
	50	8,0	42,0
	25	—	~25,0
6,8	250	—	—
	180	60,0	120,0
	125	30,0	95,0
	50	3,0	47,0

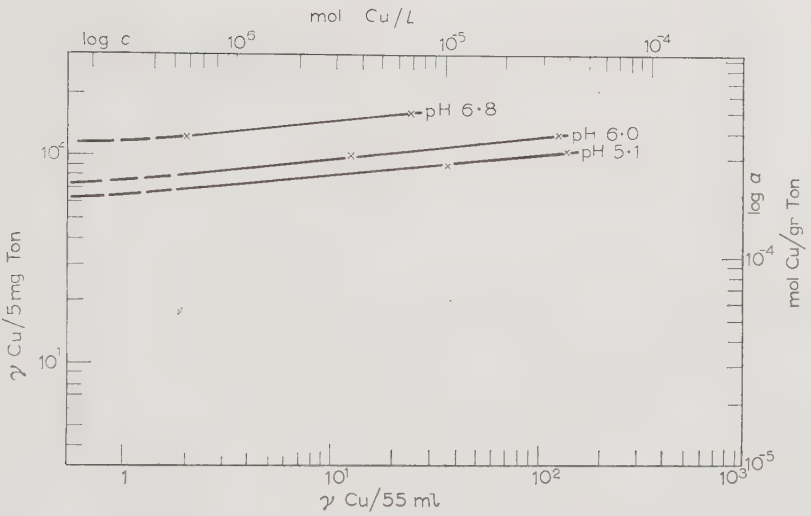


Fig. 9. Adsorptionsversuche an Montmorillonit H-25

Tabelle 9

pH	Anfangskonz. (γ Cu/55 ml)	Endkonz. (γ Cu/55 ml)	ads. Menge (γ Cu/5 mg Ton)	ads. Menge (γ Cu/m^2)
5,1	250	147,0	103,0	26,9
	125	36,0	89,0	23,2
	50	—	~50,0	13,0
6,0	250	125,0	125,0	32,6
	125	25,0	100,0	26,1
	50	—	~50,0	13,0
6,8	250	—	—	—
	180	24,0	156,0	40,7
	125	2,0	123,0	32,1
	50	—	~50,0	13,0

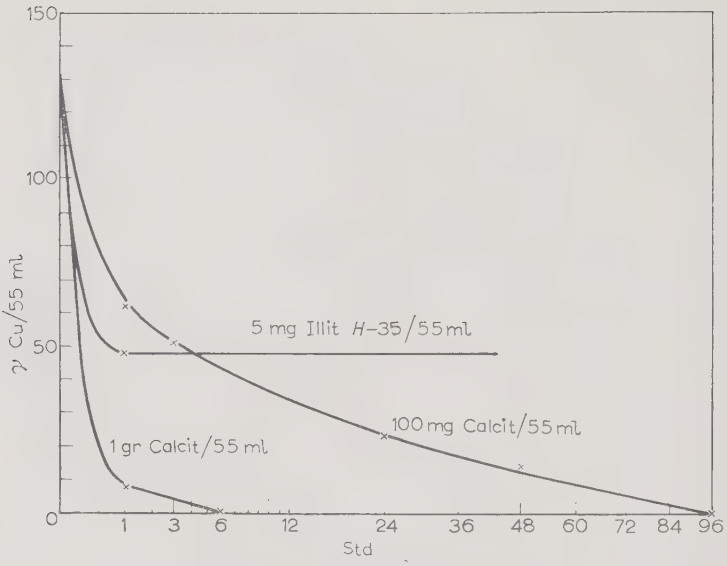


Fig. 10. Die Änderung der Kupferkonzentration mit der Zeit, Calcit und Illit H–35 als Adsorber.

Tabelle 10. Adsorptionswerte für Kaolinit Westerwald KW 2, Quarz Q 1 und Quarz Q 2 bei pH 6

Probe	Anfangskonz. (γ Cu/55 ml)	Endkonz. (γ Cu/55 ml)	ads. Menge (γ Cu/5 mg Ton)
KW2	250	232,0	18,0
	125	111,4	13,6
	50	40,2	9,8
	25	17,8	7,2
	14	8,5	5,5
Quarz Q 1	250		3,2
	125		3,0
	50		2,7
	25		2,4
	14		2,1
Quarz Q 2	250		1,6
	125		1,5
	50		1,4

oder in logarithmischer Form:

$$\log a = \log \alpha + 1/n \log c$$

x = adsorbierte Menge
m = Gewicht des Adsorbens
a = adsorbierte Menge pro Gewichtseinheit
c = Gleichgewichtskonzentration
α = Proportionalitätskonstante
$1/n$ = Konstante

$1/n$ ist nur im Gültigkeitsbereich der Freundlich'schen Isotherme eine Konstante, bei grossen Verdünnungen kann sie aber konzentrationsabhängig werden und nähert sich dann dem Wert $1/n = 1$. In diesem speziellen Fall ist dann das Henry'sche Gesetz erfüllt. Es besagt, dass die adsorbierte Menge der in der Ausgangslösung enthaltenen proportional ist. Auch die Erreichung eines Sättigungswertes wird durch die Freundlich'sche Isotherme nicht erklärt. Beide Grenzfälle, die der Erreichung eines Sättigungswertes und der Übergang in den Gültigkeitsbereich des Henry'schen Gesetzes, wurden aber hier bei den Versuchen erreicht.

Die Langmuir'sche Adsorptionsisotherme schliesst nun sowohl das Henry'sche Gesetz als auch die Erreichung eines Sättigungswertes als Grenzfälle ein. Sie lautet:

$$a = A \frac{c}{c + B}$$

a = die pro Oberfläche adsorbierte Menge
c = die Gleichgewichtskonzentration
A und B sind Konstanten

In Gebieten sehr geringer Konzentrationen wird $a \simeq c \cdot A/B$ also der Gleichgewichtskonzentration proportional, während zu grösseren Konzentrationen hin $c \gg B$ wird und damit $a =$ konstant ($\simeq A$).

Es ist nun bemerkenswert, dass bei den hier durchgeführten Adsorptionsversuchen eine Gesetzmässigkeit in Form einer Adsorptionsisotherme gilt, denn diese wurde ursprünglich für das Adsorptionsgleichgewicht an der Grenzfläche fest-gasförmig aufgestellt, also für Vorgänge, bei denen wohl nur van der Waals'sche Kräfte wirken, während die hier stattfindenden Oberflächenanlagerungen durch die stärkeren und weiter reichenden elektrostatischen Kräfte der Ionen hervorgerufen werden. Ausserdem handelt es sich hier nicht nur um reine Adsorption der Ionen, sondern um eine sogenannte Ionenaustauschadsorption (nach Griesbach, 1956). Sie ist kennzeichnend für die Wechselwirkung zwischen Elektrolyten und heteropolaren Adsorbenten. Diese austauschende Adsorption beruht auf der Gleichgewichtseinstellung der verschieden stark adsorbierbaren Ionen, die sich in der Lösung und an der Adsorberoberfläche befinden. Dass es sich tatsächlich um einen Austausch von bereits adsorbierten Ionen gegen solche aus der Lösung handelt, wurde in verschiedenen Arbeiten experimentell bestätigt.

Zu (3) die Abhängigkeit vom pH ist am stärksten bei den Kaolinmineralen und am geringsten bei den Montmorilloniten. Die Illite und das Fireclay-Mineral bilden Übergange.

Ergebnisse, spezieller Teil

Die Kaolinitproben (KZ, KW 0,6, KW 2) (Tabelle 3, 4, 10, und Fig. 3, 4, 2) sind in ihrem Verhalten sehr ähnlich trotz ihrer verschiedenen morphologischen Ausbildung. Bei niedrigem pH ist die Adsorptionszunahme mit steigender Kupfer konzentration klein, sie nähert sich beim pH = 5 einem Sättigungswert von 7–10 mäq/100 g Tonsubstanz (0,12–0,16 mäq/100 m²). Beim pH = 6 liegt der Grenzwert bei 20–25 mäq/100 g Ton (0,33–0,42 mäq/100 m²). Die höchsten Werte, die für die Kaolinite bei pH = 6,8 gemessen wurden, liegen bei 30 mäq/100 g Ton (0,5 mäq/100 m²). Es ist bemerkenswert, dass die hier gemessenen Werte für das Kationenaustauschvermögen weit höherliegen als die in der Literatur angegebenen, die in der Grössenordnung von 3–15 mäq/100 g Ton liegen. Sie beziehen sich dann allerdings meistens auf das Basenaustauschvermögen mit den Kationen Ca^{++}, Mg^{++}, Ba^{++} und NH_4^+. Die starke pH-Abhängigkeit zeigt sich deutlich durch die Zunahme des Adsorptionsvermögens bei der Gleichgewichtskonzentration von 50 γ Cu/55 ml Lösung (Tabelle 11) von 0,06 mäq/100 m² bis 0,35 mäq/100 m².

Das Fireclay-Mineral (FC) (Tabelle 5 und Fig. 5) adsorbiert grössere Mengen Kupfer unter den gleichen Bedingungen. Doch liegt hier das Kationenaustauschvermögen auf die Oberfläche umgerechnet in derselben Grössenordnung wie bei den Kaoliniten. Nur beim pH = 5,1 lässt sich ein Sättigungswert noch extrapolieren. Er liegt bei etwa 17 mäq/100 g Ton (0,16 mäq/100 m²). Der höchste bei pH = 6,8 gemessene Wert ist mit 0,41 mäq/100 m² den Daten des geordneten Kaolinites ähnlich. Auch die pH-Abhängigkeit zeigt ein ähnliches Verhalten.

Die Illite (H-35. H-36) (Tabelle 6, 7, Fig. 6, 7) bilden den Übergang von den Kaolinmineralen zu den stark adsorbierenden Montmorilloniten. Die Abhängigkeit von der Kupfer konzentration und den pH-Änderungen ist auch hier noch erheblich. Es lässt sich ein Sättigungswert nicht mehr extrapolieren, er wird erst bei höheren Kupfer konzentrationen erreicht werden. Berechnet man jedoch das Kationenaustauschvermögen auf die Oberfläche um, so ergibt sich die Tatsache, dass die Werte auf 100 m² bezogen niedriger sind als bei den Kaolinmineralen. Für den Illit H-35, dessen Oberfläche bestimmt wurde, ist der höchste gemessene Wert beim pH = 6,8 42,5 mäq/100 g Ton oder 0,22 mäq/100 m².

Die Montmorillonite (H-19, H-25) (Tabelle 8, 9; Fig. 8, 9) adsorbieren das Kupfer aus der Lösung am stärksten. Dies war auf Grund der Äthylenglykoladsorption zu erwarten. Auch die in der Literatur angegebenen Werte für das Basenaustauschvermögen sind für die Montmorillonite stets am grössten. Für die Na-Montmorillonite aus Wyoming werden 95 mäq/100 g bei 105°C getrockneter Substanz angegeben, für die Ca-Montmorillonite aus Mississippi sogar 160 mäq/100 g bei 105°C getrocknetem Ton. Auf Grund dieser Daten müsste eigentlich die Adsorptionskapazität des Ca-Montmorillonites H-19 höher sein als die des Na-Montmorillonites H-25. Leider verklebten sich die Blättchen der feinen Fraktion von Probe H-19 durch das Trocknen an der Luft zu Aggregaten, die sich auch durch längeres Schütteln mit Wasser nicht wieder disperigeren liessen, was bei Ca-Montmorilloniten häufig beobachtet wird. Es

wurden deswegen nur Oberflächenbestimmungen für die Probe H-25 durchgeführt und damit nur für diesen Ton das Basenaustauschvermögen, auf die Oberfläche bezogen, berechnet. Der höchste Wert liegt bei 0,13 mäq/100 m^2, entsprechend 95,6 mäq/100 g Ton.

Zum Vergleich seien hier noch einmal die Kupferadsorptionswerte für eine Gleichgewichtskonzentration von 50 γ Cu/55 ml in Milliäquivalent pro 1 g und pro 100 m^2 in Abhängigkeit vom pH angegeben.

Tabelle 11

Probe	KW 0,6		KZ		FC		H-35		H-25	
pH	(mäq/ 1 g)	(mäq/ 100 m^2)	(mäq/ 1 g)	(mäq/ 100 m^2)	(mäq/ 1 g)	(mäq/ 100 m^2)	(mäq/ 1 g)	(mäq/ 100 m^2)	(mäq/ 1 g)	(mäq/ 100 m^2)
5,1	0,03	0,05	0,03	0,06	0,04	0,07	0,08	0,04	0,59	0,08
6,0	0,07	0,12	0,07	0,12	0,07	0,12	0,15	0,08	0,74	0,10
6,8	0,17	0,29	0,20	0,35	0,19	0,33	0,42	0,22	(1,10)	(0,15)

Die Werte (1,10) und (0,15) für H-25 wurden extrapoliert.

Ausser den Tonmineralen wurden noch Messungen an Quarzen und Calcit durchgeführt.

Für die Quarzproben (Q1, Q2) (Tabelle 10, Fig. 2) gilt, wie aus der graphischen Darstellung im doppeltlogarithmischen Maßstab hervorgeht, ebenfalls die Freundlich'sche Isotherme. Der mit Methanol geschlämmte Quarz Q1 zeigt das grössere Adsorptionsvermögen gegenüber dem mit NH_4OH-haltigem Wasser aufbereitetem Quarz Q2. Da hier die adsorbierten Kupfermengen sehr klein sind, ist es schwer zu entscheiden, wie weit der Unterschied im Adsorptionsvermögen reell ist. Es liesse sich durch die verschiedene Vorbehandlung erklären.

Das Verhalten des Calcit in wässrigen Lösungen mit den Kupfer-Ionen ist vollkommen anders als das der Tonminerale (Tabelle 12 und Fig. 10). Untersucht man die Abhängigkeit der Kupfer konzentration in der Lösung mit der Zeit, so stellt sich weder nach 1 Std nochnach 24 Std ein stabiles Gleichgewicht ein, wie es bei den Tonmineralen und den Quarzproben der Fall ist. Die Kupfer konzentration nimmt vielmehr kontinuierlich in der Lösung ab und nähert sich unendlich kleinen Werten. Hier darf man nicht mehr von austauschender Adsorption sprechen. Es handelt sich um eine chemische Reaktion zwischen dem $CuSO_4$ und dem Karbonat (Garrels und Dreyer, 1952).

Die Versuche wurden beim pH = 7 in der üblichen Weise durchgeführt. Zum Vergleich des unterschiedlichen Verhaltens wird der Illit H-35 mit angeführt.

Canals und Marignan (1949, 1950) nehmen bei ihren Untersuchungen des Systems Kupferlösung—Kalk reine Adsorption an. Die $CuSO_4$-Konzentration in der Lösung von $2–5 \cdot 10^{-7}$ g–Atom/l und einer zugegebenen Menge von 50 mg $CaCo_3$/l sind in ihren Versuchen etwas niedriger gehalten als in den hier durchgeführten. Trotz der etwas veränderten Bedingungen ist kaum

anzunehmen, dass es sich in diesem Fall um reine Adsorption handelt und um keine chemische Reaktion.

Correns (1924) konnte bei seinen Untersuchungen keine Adsorption des Kupfers an Calciumkarbonat feststellen. Seine anderen Versuchsergebnisse über die Adsorption von Kupfer an Kaolin von Kahlbaum stehen in guter Übereinstimmung mit den hier gemessenen Werten für das Basenaustauschvermögen der Kaolinminerale, allerdings nur so lange die Gleichgewichtskonzentration

Tabelle 12. Kupferkonzentration (γ/55 ml)

Probe	(mg/55 ml)	0 Std	1 Std	3 Std	6 Std	24 Std	48 Std	96 Std
$CaCO_3$	100	130	62	52	—	24	15	0
	1000	130	8	—	0			
Illit H-35	5	130	82	—	82			

nicht wesentlich höher als 50 γCu/55 ml Lösung ist. Bei höheren Konzentrationen wurde von Correns ein Maximum in dem Verlauf der Isotherme festgestellt. Dieses tritt bei solchen Kupferkonzentrationen und pH-Werten auf, wo man mit einer Ausfällung basischer Kupfersalze aus der Lösung schon rechnen muss.

Diskussion der Ergebnisse

Die wichtigste Frage, die sich erhebt, wenn man versucht, die Ergebnisse der experimentellen Untersuchungen zu deuten, ist die nach der Art der Adsorption, die den hier beschriebenen Vorgängen zu Grunde liegt, und nach den Kräften. Es kann hier nicht auf das Problem der Ionenadsorption im allgemeinen eingegangen werden, dafür muss auf die reichhaltige Literatur hingewiesen werden (Nachod, 1949).

In dem speziell hier untersuchten System wurden von den Tonmineralen Kationen mit der Lösung ausgetauscht. Im Falle einer reinen Ionenanlagerung wird das Kation zwar stark angezogen nicht aber aus seiner Hydrathülle gerissen werden. Handelt es sich dagegen um eine Kationenadsorption im engeren Sinne, so tritt eine vollständige Vereinigung des Kations mit den Partikeln der Adsorberoberfläche unter Bildung einer höchstens monomolekularen Schicht ein.

Beide Arten der Adsorption setzen negative nicht abgesättigte Ladung im Gitter voraus Solche negative Überschussladung kann bei den Tonteilchen folgende Ursachen haben:

(1) Substitution durch niedriger wertige Ionen, z.B. Al^{3+} durch Mg^{2+} in den Oktaederschichten und in geringerem Umfang von Si^{4+} durch Al^{3+} in den Tetraederschichten.

(2) Dissoziation des H^+ aus einigen OH-Gruppen, die von aussen zugänglich sind.

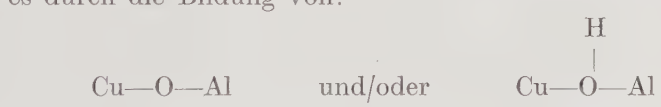
(3) Unabgesättigte Ladungen, die auf zerbrochenen Bindungen an den seitlichen Begrenzungsflächen der Kristalle beruhen.

Die unter (2) und (3) erwähnten Möglichkeiten lassen sich in ihrer

Wirkungsweise wohl kaum scharf voneinander trennen. Sie werden deshalb meistens zusammen besprochen.

Beim Montmorillonit kann man annehmen, dass die Substitution Al durch Mg am wichtigsten für die Erklärung des Basenaustauschvermögens ist. Dass dieser Ersatz stattfinden kann, wurde durch Montmorillonit-Analysen bestätigt (Jasmund, 1955). Schon ein Verhältnis von 10 Al : 1 Mg in der Oktaederschicht bildet eine solche negative Überschussladung im Gitter, dass sich allein dadurch ein Basenaustauschvermögen von 100 mäq/100 g Ton ergeben würde. Die adsorbierten Kationen befinden sich damit in den Zwischenschichten, wie die Röntgenanalysen durch die Veränderung des 001 Reflexes bei verschiedener Kationenbelegung wahrscheinlich macht.

Die pH-Abhängigkeit liesse sich dagegen folgendermassen erklären. Beim Adsorptionsvorgang stehen Cu^{2+}- und H^{+}-Ionen der Lösung mit den Ionen am Adsorber in Konkurrenz. Wird nun die H^{+}-Ionenkonzentration erniedrigt, d.h. der pH-Wert erhöht, so können jetzt mehr Kupfer-jonen den Platz von H^{+} am Gitter einnehmen, d.h. mit steigendem pH wird die Kupfer adsorption grösser. Dass ein solcher Austausch stattfinden kann, vermuteten DeMumbrum und Jackson (1956). Sie untersuchten deshalb das Infrarot-Adsorptions-Spektrum von Montmorillonit und kupfergesättigtem Montmorillonit. Sie stellten fest, dass der Ausschlag bei 2,8 μ, der charakteristisch ist für die Valenzschwingung der Hydroxylgruppen im Gitter, durch die Behandlung des Montmorillonites mit Kupfer geringer wurde, die Intensität der Bande nahm um etwa 25% ab. Stattdessen traten bei 6,4 μ und 7,0 μ zusätzliche Ausschläge auf. Die Autoren versuchten es durch die Bildung von:



zu erklären.

Bei den Kaolinmineralen ist der Effekt durch die Substitution wahrscheinlich gering. Doch schon ein Ersatz von 0,25% Si durch Al würde ein Basenaustauschvermögen von 2 mäq/100 g Ton (Schofield, 1953) hervorrufen. Dies kann natürlich nicht durch chemische Analysen bewiesen werden, da es im Rahmen der Fehlergrenze liegt. Für die Kaolinminerale bleiben als Erklärung für die Adsorption hauptsächlich die unter (2) und (3) erwähnten Möglichkeiten.

Vielfach wird das Basenaustauschvermögen nur durch die an den Kristallbruchflächen entstehenden negativen Ladungen erklärt. Man versucht diese Theorie experimentell zu stützen, indem man Tone durch Zermahlen in der Kugelmühle zerkleinert und dabei die Zunahme der Ionenadsorption beobachtet. Mortland und Erickson (1956) führten solche Versuche unter gleichzeitiger Bestimmung der jeweils gebildeten Oberflächen nach der Äthylenglykolmethode durch. Es zeigt sich, dass trotz starker Zerstörung der Kristalle die Austauschfähigkeit (auf 100 m^2 umgerechnet) nicht grösser wird, wie es vermutet wurde.

Auch ein Vergleich der Oberflächenausbildung mit dem Austauschvermögen der hier verwendeten Proben von Kaolinmineralen zeigen ebenfalls, dass ein Kaolinit KW (Abb. 2) mit viel Seitenfläche genau so stark adsorbiert wie ein Kaolinit KZ (Abb. 1), der verhältnismässig grosse gut ausgebildete Kristalle

besitzt. Damit wird die alleinige Erklärung der Adsorption durch die Seitenflächenladungen unglaubwürdig.

Es wird sich hier für die Adsorption beim Kaolinit, wie z.T. auch beim Montmorillonit, um eine Wechselwirkung zwischen Cu^{2+} und H^+ handeln. Damit wäre gleichzeitig die starke pH-Abhängigkeit erklärt. Auch bei Kaoliniten haben DeMumbrum und Jackson (1956) das Infrarot–Adsorptions–Spektrum aufgenommen. Es zeigt bei 2,8 μ wieder die charakteristische OH-Valenzschwingung. Wird der Kaolinit mit Kupfer-Jonen gesättigt, so erniedrigt sich, wie beim Montmorillonit, die Intensität dieser Bande. Zur Erklärung wird man dieselben Möglichkeiten, wie sie beim Montmorillonit erwähnt wurden, diskutieren müssen.

Es bleibt jetzt noch die Frage, warum das Kupfer-Jon soviel stärker adsorbiert wird als andere ein- und zweiwertige Kationen, wie es ja aus den unterschiedlichen Werten für das Basenaustauschvermögen hervorgeht.

Auf Grund der Röntgenaufnahmen von kupfergesättigtem Montmorillonit H-25 ergibt sich ein Schichtebenenabstand (001) von etwa 12,4 Å, der des Na-gesättigten liegt bei 12,2 Å. Für Mg- und Ca-gesättigten Montmorillonit gibt Bradley 14 Å an. Daraus lässt sich schliessen, dass das hydratisierte Kupfer-Jon fast denselben Raum in den Zwischenschichten einnimmt, wie das hydratisierte Natrium-Jon. Das Kupfer hydrat trägt aber gegenüber dem Natriumhydrat die doppelte Ladung, wird also deshalb stärker adsorbiert werden wie dieses und wird auch noch mit mehr H^+-Ionen in Austausch treten (Mitra und Rajagopalan, 1952).

Auf eine andere Erklärungsmöglichkeit weisen Bower und Truog (1940) hin und Mensel und Jackson (1950). Sie stellten fest, dass neben Kupfer auch noch eine Reihe anderer polyvalenter Kationen ein sehr viel höheres Austauschvermögen im Vergleich zu den Alkalien zeigen. Es handelt sich bei allen diesen Kationen um schwache Basenbildner, also Kationen, die teilweise hydrolisiert sein können. Für Kupfer gilt (Hagisawa, 1939):

$$Cu^{++} + H_2O = Cu(OH)^+ + H^+$$

Bei der Adsorption wird ein Mol dieses $Cu(OH)^+$ nur noch ein Äquivalent der Basenaustauschfähigkeit besetzen, während ein Mol nicht hydrolysiertes Cu^{++} zwei Äquivalente absättigte, entsprechend seiner Ladung. So liesse sich ein erhöhtes Austauschvermögen auch erklären. Es fehlen aber leider genauere quantitative Daten über die Bildung von $Cu(OH)^+$ und damit über deren möglichen Einfluss auf den Adsorptionsmechanismus.

Schlussbemerkungen

Wie weit können nun auf Grund der Ergebnisse dieser Arbeit solche Adsorptionsprozesse zur Lösung geochemischer Fragen herangezogen werden? Nach den hier vorliegenden Messdaten liessen sich noch Kupfer gehalte von 3% (30000 g Cu/t) auf solche Vorgänge zurückführen. Voraussetzung für diesen experimentell gefundenen Höchstwert ist allerdings Montmorillonit als Adsorbens und eine Kupfer konzentration im Wasser von mindestens 400 γ Cu/l. Solche extrem hohen Kupfer gehalte werden jedoch in der Natur kaum vorkommen. In

natürlichen Wässern, Meeren, Flüssen und Seen liegen die Werte viel niedriger, meist in der Grössenordnung von 1–15 γ Cu/l. KRAUSKOPF (1956) nimmt an, dass grosse Teile des in Lösung gehenden Kupfers durch Adsorption an die sedimentierende Tontrübe fixiert werden. Er erklärt hierdurch den niedrigen Kupfer gehalt im Meerwasser. Eine Stütze für diese Annahme ist die Tatsache, dass marine Tone relativ hohe Kupfer gehalte haben können. WEDEPOHL (1957) fand bei seinen Untersuchungen als Durchschnittswerte in Tonen der Flachsee 45 g Cu/t, in Tiefseetonen des Atlantik 120 g Cu/t und in den Tiefseetonen des Pazifik 320 g Cu/t. Wie die experimentellen Befunde der vorliegenden Arbeit zeigen, können solche Kupfer mengen in Tonen sich ohne weiteres durch Adsorption abgeschieden haben.

Im Kupferschiefer beträgt der Gehalt an Kupfer bis etwa 3% (30000 g Cu/t). Nach der meist angeführten Meinung wird die Abscheidung des Kupfers im Kupferschiefer auf chemische Ausfällung des Kupfers durch H_2S in bodennahen Bereichen des Meerwassers zurückgeführt. (Löslichkeit von $CuS = 5 \cdot 10^{-20}$g/100 ml, pH = 7,20°C) (GARRELS, 1944). Die vorliegenden Messdaten lassen es aber als möglich erscheinen, dass auch hier die Adsorption eine Rolle gespielt hat. Eine qualitative Voruntersuchung einiger Kupferschieferproben mit dem Beugungsgoniometer ergab als Mineralbestand neben Calcit und Quarz vor allem Illit und Minerale der Kaolingruppe als Tonminerale. Diese Tonminerale allein können niemals Kupfer gehalte von 3% im Sediment erklären. Eine Adsorption könnte aber gleichzeitig mit der Sulfidbildung stattgefunden haben. Eine mögliche Mitwirkung dieser Vorgänge könnte sich so abgespielt haben, dass Kupfer durch Adsorption an die Tonminerale angelagert und mit diesen abgelagert wurde. Im Sediment wurde durch die Verwesung der gleichzeitig mitabgelagerten organischen Substanz, die auch bei der Adsorption vielleicht schon mitwirkte, H_2S produziert, durch welches das vorher adsorbierte Kupfer im Lauf der Diagenese in Sulfid umgewandelt wurde.

Anerkennung—Zum Schluss der Arbeit möchte ich meinem verehrten Lehrer Herrn Prof. Dr. C. W. CORRENS sehr herzlich danken für die Überlassung des Themas und die vielen wertvollen Anregungen während der Durchführung der Arbeit. Auch Fräulein Dr. SCHNEIDERHÖHN, Herrn Dozenten Dr. K. H. WEDEPOHL und Herrn Dr. F. LIPPMANN danke ich für zahlreiche Hinweise und manche praktische Hilfe. Besonderer Dank sei noch Herrn Dr. SCHLOTE für die Anfertigung der elektronenoptischen Aufnahmen gesagt.

ZUSAMMENFASSUNG

Es wurden Versuche über die Kupfer adsorption sowohl an verschiedenen Tonmineralen wie an Quarz und Calcit in Abhängigkeit von pH und Kupfer konzentration durchgeführt. Als Tonminerale wurden die feinsten Fraktionen von zwei Kaolinitproben, einer Fireclay-Mineralprobe, zweier Illitproben und zweier Montmorillonitproben verwendet. Die Oberflächenbeschaffenheit dieser Proben wurde teilweise durch elektronenoptische Aufnahmen und auch durch die Methode der Äthylenglykoladsorption genauer bestimmt.

Allgemein lässt sich sagen, dass die Adsorption des Kupfers an den Tonmineralen und am Quarz nach der Freundlich, schen Isotherme verläuft, dagegen findet beim Calcit eine chemische Reaktion statt. Das Adsorptionsvermögen der Tonminerale nimmt mit steigender Kupfer konzentration und

steigendem pH zu. Der Einfluss der Konzentration und des pH ist bei den Kaoliniten am stärksten bemerkbar, bei den Montmorilloniten ist er viel geringer. Das Adsorptionsvermögen, bezogen auf 100 g Ton, zeigt steigende Werte vom Kaolinit über Fireclay-Mineral und Illit zum Montmorillonit. Bezieht man es aber auf die Oberflächeneinheit, Adsorptionsvermögen pro 100 m^2, so liegen die Werte für Kaolinit und Fireclay-Mineral in derselben Grössenordnung, während Illit und Montmorillonit teilweise ein viel kleineres Adsorptionsvermögen haben.

Auf die Bedeutung solcher Adsorptionsprozesse für geochemische Fragen wird kurz eingegangen.

Literatur

Alexanien C. (1956) Dickenmessungen der sogenannten amorphen Quarzschicht durch Elektronenbeugung. *C. R. Acad. Sci.*, Paris **242,** 2145.

Bloch J. M. und Charbonelle J. (1955) Obtention et êtudes de montmorillonit cuivre. *Bull. Soc. Chim. Fr.* 511.

Borland J. W. und Reitemeier R. F. (1950) Kinetic exchange studies on clay with radioactive Ca. *Soil Sci.* **69,** 251–260.

Bower C. A. und Truog E. (1940) Base exchange capacity determination as influenced by nature of cation employed and formation of basic exchange salts. *Proc. Soil Sci. Soc. Amer.* **5,** 86.

Bower C. A. und Gschwend F. B. (1952) Ethylene glycol retention by soils as a measurement of the surface area and interlayer swelling. *Proc. Soil Sci. Soc. Amer.* **16,** 342.

Brown E. A. (1946) Nomographic procedure for a two-component coloured system. *Industr. Engng. Chem.* (*Anal.*) **18,** 493.

Brunauer S., Emmett P. H. und Teller E. (1938) Adsorption of gases in multimolecular layers. *J. Amer. Chem. Soc.* **60,** 309–319.

Canals M. M., Marignan R. und Cordier S. (1949–50) Adsorption de quelques ions metalliques en solution très diluée. *Ann. Pharm. Franç.* **7,** 502; **8,** 368.

Clays and Clay Minerals. Proceedings of the Third National Conference on Clays and Clay Minerals. Publ. 395, National Academy of Science, Washington D.C. 1955.

Correns C. W. (1924) Adsorptionsversuche mit sehr verdünnten Kupfer- und Bleilösungen und ihre Bedeutung für die Erzlagerstättenkunde. *Kolloidzschr.* **34,** 341–349.

Davis L. E. (1945) Simple kinetic theory of ionic exchange for ions of unequal charge. *J. Phys. Chem.* **49,** 473.

Dyal R. S. und Hendricks S. B. (1950) Total surface of clays in polar liquids as a characteristic index. *Soil Sci.* **69,** 421–432.

Dyal R. S. und Hendricks S. B. (1956) Formation of mixed layer minerals by potassium fixation in montmorillonite. *Proc. Soil Sci. Soc. Amer.* **16,** 45.

Fischer H. (1937) Dithizonverfahren in der chemischen Analyse Überlick über die Entwicklung der letzten Jahre. *Angew. Chem.* **50,** 919–932.

Freundlich H. (1930) *Kapillarchemie.* Akademische Verlagsgesellschaft, Leipzig.

Garrels R. M. (1944) Solubility of metalsulfides in dilute vain forming solutions. *Econ. Geol.* **39,** 472.

Garrels R. M. und Dreyer R. M. (1952) Mechanism of limestone replacement at low temperatures and pressures. *Bull. Geol. Soc. Amer.* **63,** 325–379.

Gaudin A. M., Spedden H. R. und Laxen P. A. (1952) Adsorption of sodium on quartz. *Min. Engng.* **4,** 693–696.

Goates F. R. und Anderson K. (1956) Saure Eigenschaften von Quarz. *Soil Sci.* **81,** 277.

Griebach R. und Richter A. (1956) Ionenaustauscher als hochdisperse Systeme und ihre Wirkung auf kolloide Stoffe. *Kolloidzschr.* **146,** 107.

Grim R. E. (1953) *Clay Mineralogy.* McGraw-Hill, New York.

Hagisawa H. (1939) Measurements of pH by means of the glass electrode and the hydrolysis of copper sulfate. *Bull. Inst. Phys. Chem. Res., Tokyo* **18,** 275.

Heide F. und Singer E. (1954) Der Gehalt des Saalewassers an Kupfer und Zink. *Naturwissenschaft* **21,** 498.

Jasmund K. (1950) Texturaufnahmen von blättchenförmigen Mineralen. *Neues Jb. Miner., Mh.* **3,** 63–72.

Jasmund K. (1955) *Die silicatischen Tonminerale.* Verlag Chemie, Weinheim Bergstr.

Jenny H. (1936) Kinetic theory of ionic exchange. *J. Phys. Chem.* **40,** 511.

Kohler E. (1903) Adsorptionsprozesse als Faktoren der Lagerstättenbildung und Lithogenesis. *Z. prakt. Geol.* **5,**49.

Krauskopf K. B. (1956) Factors controlling the concentration of thirteen rare metals in sea water. *Geochim. et Cosmochim. Acta* **9,** 1–32.

Kulp J. L. und Carr D. R. (1952) Oberflächen von Tiefseesedimenten. *J. Geol.* **60,** 148.

Lippmann F. (1952) Mineralogische Untersuchungen an einigen niederhessischen Tertiärtonen. *Heidelberg. Beitr. Min.* **3,** 219–252.

Menzel R. G. und Jackson M. L. (1950) Mechanism of sorption of hydroxy cupric ion by clays. *Proc. Soil Sci. Soc. Amer.* **15,** 122.

Mitra S. P. und Phabam Prakash (1957) Adsorption of potassium as influenced by concentration and pH of the solution. *Soil Sci.* **83,** 151.

Mitra R. P. und Rajagopalan K. S. (1952) Origin of the base-exchange capacity of clays and significance of its upper limiting value. *Soil Sci.* **73,** 349.

Morel R. (1955) Über die Bilanz der Adsorption von Kationen verschiedener Grösse durch die Tone. *C. R. Acad. Sci., Paris* **239,** 1846.

Mortland M. M. und Erickson A. E. (1956) Surface reactions of clay minerals. *Proc. Soil Sci. Amer.* **20,** 476.

DeMumbrum L. E. und Jackson M. L. (1956) Infra-red adsorption evidence on exchange reaction mechanism of copper and zinc with layer silicate clays and peat. *Proc. Soil Sci. Soc. Amer.* **20,** 334.

DeMumbrum L. E. und Jackson M. L. (1956) Copper and zinc exchange from dilute neutral solutions by soil colloidales electrolytes. *Soil Sci.* **81,** 353.

Nachod F. C. (1949) *Ion Exchange.* Academic Press, New York.

Nahin P. G. (1955) Infra-red analysis of clays and related minerals. *Clays and Clay Technology Bull.* **169,** 112.

Nelson R. und Walton H. F. (1944) Cation exchange at high pH. *J. Phys. Chem.* **48,** 406.

Clay Minerals. R.P.I. Research Project 49, Columbia University, New York (1951).

Sandell E. B. (1950) *Colorimetric Determination of Traces of Metals.* Interscience, New York.

Schofield R. K. und Samson H. R. (1953) The deflocculation of kaolinite suspensions and the accompanying change-over from positive to negative chloride adsorption. *Clay Min. Bull.* **2,** No. 9, 45–51.

Stöber W. (1956) Adsorptionseigenschaften und Oberflächenstrukturen von Quarzpulvern. *Kolloidzschr.* **145,** 17.

Thiessen P. A. (1942) Wechselseitige Adsorption von Kolloiden. *Z. Elektrochem.* **48,** 675.

Turekian K. K. und Kleinkopf M. D. (1956) Estimates of the average abundance of Cu, Mn, Pb, Ti, Ni and Cr in surface waters of Maine. *Bull. Geol. Soc. Amer.* **67,** 1129.

Wedepohl K. H. (1957) Ein Vergleich von Tiefsee- und küstennah abgelagerten Tonen in einigen Spurenelementen. (Vortragsreferrat). *Symposium on Geochemistry within the Sixteenth International Congress, Pure and Applied Chemistry, Paris.*

Geochimica et Cosmochimica Acta, 1959, Vol. 15, pp. 330 to 336. Pergamon Press Ltd. Printed in Northern Ireland

Contribution to the lognormal distribution of elements

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Abstract—This paper contains a discussion on the equation expressing the course of the density of probability distribution in a lognormal distribution. A proof is given that the most probable value and the geometrical mean are two different magnitudes. Therefore the following plot must be valid:

$$\log \frac{\text{abundance}}{\text{most frequent concentration}} = 3{\cdot}4539$$

which, on the other hand differs from the plot published by Ahrens (1954a). The respective theoretical considerations are shown on the distribution of lead in Canadian granite (Ahrens, 1954).

Introduction

In studying the distribution of some trace-elements in a pyrrhotine deposit at Helpa (Central Slovakia) it was stated that the distribution of these elements was lognormal (Ďurovič, 1957). The histograms were drawn by means of about 200 polarographic determinations of nickel, zinc, copper and manganese. On discussing the original histograms, i.e. those which are not transformed into a logarithmic scale, it was found that the geometrical mean never quite complies with the most frequent value of concentration which might be expected from the result of Ahrens's works (1954). In order to explain this discrepancy one first considers histograms relating to the distribution of trace-elements, brought by Ahrens (1954). In the majority of these histograms the above mentioned discrepancy was found. It is particularly notable in the histograms showing the distribution of lead in Canadian granite. In Fig. 1 a reproduction of Ahrens' histograms is shown.*

This example is chosen for further considerations because according to Miller and Goldberg (1955), it complies with the rules of a lognormal distribution. One may see at a first glance that the value of the most frequent concentration lies somewhere between 5 and 10 p.p.m., whereas the geometric mean equals 12, and the arithmetic mean, 15 p.p.m.

From the preceeding we may conclude that Ahrens' assertion about the identity of the value of the most frequent concentration with the value of the geometric mean in lognormal distribution is probably incorrect. Since experimental proof of that fact may not always be reliable the following theoretical method was used.

Theoretical Discussion

Let us take a multitude of values characterized by their lognormal distribution.

* The histogram, transformed into a logarithmic scale does not comply exactly with Table 1 of Ahrens's work.

Let us also suppose that this distribution is continuous, i.e. that any value of the said multitude may adopt any value in the interval from zero to infinity.*
The distribution of the logarithms related to the values forming the said multitude will be normal and of course continuous too. For the distribution of density of probabilities $p(x)$ there is the known Gaussian function:

$$p(x) = \frac{1}{\lambda\sqrt{(2\pi)}} \exp\left\{-\frac{1}{2\lambda^2}(x-a)^2\right\} \tag{1}$$

where λ represents the mean square deviation of the individual values forming the multitude from the value of their arithmetic mean. If we use formula (1) for

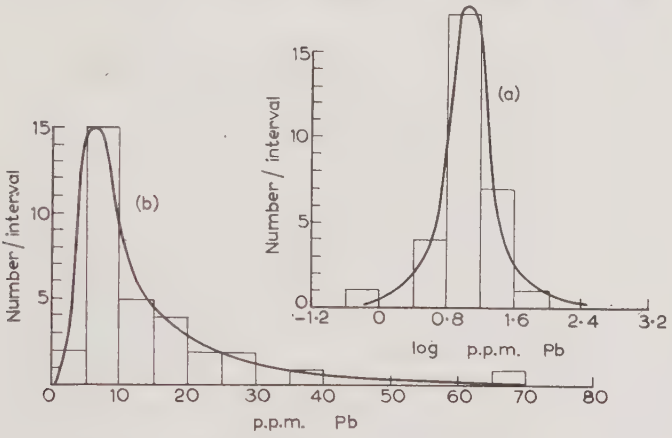

Fig. 1. Frequency distribution of lead in Canadian granite [reprinted from AHRENS's work (1954a)].

our multitude, we find that the values x are logarithms (f.i. decadic) of the original values forming the multitude and that a is their arithmetic mean, i.e. the logarithm of the geometric mean of the original values forming the multitude. We therefore may write that:

$$p(x) = \frac{1}{\lambda\sqrt{(2\pi)}} \exp\left\{-\frac{1}{2\lambda^2}(x - \log \text{g.m.})^2\right\} \tag{2}$$

If our multitude comprises a number of N values, supposing that N may be a sufficiently large number, we find that in an interval dx there will be dn values:

$$dn = Np(x)dx = \frac{N}{\lambda\sqrt{(2\pi)}} \exp\left\{-\frac{1}{2\lambda^2}(x - \log \text{g.m.})^2\right\} dx \tag{3}$$

By integrating equation (3) in limits for which we substitute gradually the extreme values of the individual intervals in the histogram which was transformed into a logarithmical scale, we obtain theoretical values of frequency in these intervals, which may be used, e.g. in evaluating the degree to which our multitude complies with the law of normal distribution.

* The distribution of concentrations of elements in any geological material is evidently continuous, because there is no reason for a restriction of values of concentration on to certain numbers.

A similar plot is to be found even for the lognormal distribution (Hald, 1952). We may find such plots by substituting the variable x in the equation (3) by its antilogarithm y according to the formula:

$$y = 10^x \Rightarrow x = \log y$$

Since

$$\log y = 0{\cdot}4343 \ln y = x$$

and

$$d \log y = \frac{1}{y} . 0{\cdot}4343\, dy = dx$$

after substituting into equation (3) we obtain:

$$dn = \frac{0{\cdot}4343\, N}{\lambda\sqrt{(2\pi)}} . \frac{1}{y} . \exp\left\{ - \frac{1}{2\lambda^2} \left(\log \frac{y}{\text{g.m.}} \right)^2 \right\} dy \tag{4}$$

According to this, the density of distribution of probabilities in lognormal distribution is expressed by the formula:

$$p^*(y) = \frac{0{\cdot}4343}{\lambda\sqrt{(2\pi)}} . \frac{1}{y} . \exp\left\{ - \frac{1}{2\lambda^2} \left(\log \frac{y}{\text{g.m.}} \right)^2 \right\} \tag{5}$$

The maximum of this function is evidently the most probable value of the multitude of values y and we obtain it by means of the first derivation of equation (5):

$$\frac{dp^*(y)}{dy} = \frac{0{\cdot}4343}{\lambda\sqrt{(2\pi)}} . \frac{1}{y^2} . \exp\left\{ - \frac{1}{2\lambda^2} \left(\log \frac{y}{\text{g.m.}} \right)^2 \right\} . \left(1 + \frac{0{\cdot}4343}{\lambda^2} [\log y - \log \text{g.m.}] \right)$$

From the above we see, that:

$$\log y_{\max} = \log \text{g.m.} - 2{\cdot}3026\lambda^2 \tag{6}$$

The last equation (6) clearly shows that in a continuous lognormal distribution the most probable value always lies lower than that of the geometric mean. Therefore Ahrens' plot must be altered in the following way: Since the equation:

$$\log \frac{\text{a.m.}}{\text{g.m.}} = 1{\cdot}1513\lambda^2 \tag{7}$$

is valid, we may write according to equation (6)

$$\log \text{a.m.} = \log y_{\max} + (2{\cdot}3026 + 1{\cdot}1513)\lambda^2 = \log y_{\max} + 3{\cdot}4539\lambda^2$$

i.e. that

$$\log \frac{\text{abundance}}{\text{most frequent concentration}} = 3{\cdot}4539\lambda^2 \tag{8}$$

As in the case of the equation (3) we may integrate equation (4) and obtain thus data needed for the theoretical histogram of the lognormal distribution. For this operation we of course require tables of probability integral. In such a case one may compare a theoretically and experimentally determined histogram, e.g. by means of Pearson's χ^2 test.

By means of equation (3) or equation (4) respectively, one may develop distribution curves which are most representative for the purpose of comparing experimentally obtained histograms with theory, since the following two approximate equations are valid:

$$\Delta n = \frac{N\Delta x}{\lambda\sqrt{(2\pi)}} \exp\left\{-\frac{1}{2\lambda^2}(x - \log \text{g.m.})^2\right\} \tag{9}$$

$$\Delta n^* = \frac{0{\cdot}4343\ N\Delta y}{\lambda\sqrt{(2\pi)}} \cdot \frac{1}{y} \cdot \exp\left\{-\frac{1}{2\lambda^2}\left(\log \frac{y}{\text{g.m.}}\right)^2\right\} \tag{10}$$

Equation (9) refers to normal distribution and equation (10) to lognormal distribution.

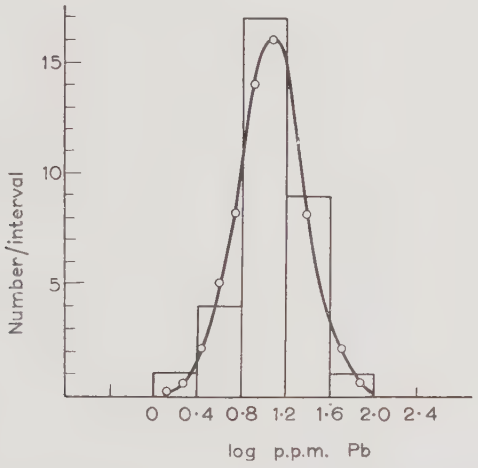

Fig. 2. Frequency distribution of lead in Canadian granite (transformed into logarithmical scale).

Practical Example

Numerical characteristics of the distribution of lead in Canadian granite are the following:

$$\text{a.m.} = 15 \text{ p.p.m.}, \quad \text{g.m.} = 12 \text{ p.p.m.}, \quad \lambda = 0{\cdot}32$$

Inserting those values by substitution into equation (6) we obtain

$$\log y_{\max} = \log 12 - 2{\cdot}3026.\ (0{\cdot}32)^2 = 0{\cdot}843$$

$$y_{\max} = 6{\cdot}96 \text{ p.p.m.} \doteq 7 \text{ p.p.m.}$$

Figures 2 and 3 show that this value is in very good accordance with the histograms into which the distribution curves are inserted according to equations (9) and (10) respectively.

The curves shown on Fig. 2 and Fig. 3 are somewhat different from those reported by Ahrens (1954). First of all we see that the lognormal curve developed

according to equation (10) differs essentially from the one reported by Ahrens, which is doubtless a sign of the fact that the latter curve was obtained without any theoretical basis.

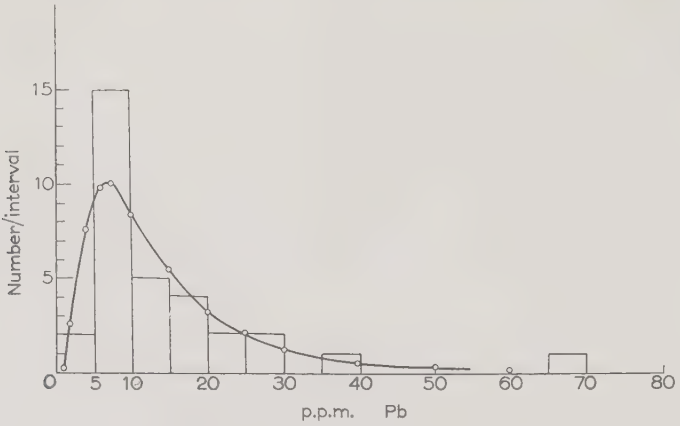

Fig. 3. Frequency distribution of lead in Canadian granite (original distribution).

Discussion

Calculations mentioned in the preceeding sections clearly showed that in a continuous lognormal distribution there is no identity between the mode (the most likely value of the multitude) and the geometric mean. If nevertheless we read through the literature cited by Ahrens, we find first of all Gaddum's work (1945) and then discussions by Hancock (1948a, b) and Dunkin (1948) which all consider the same problem. To cite a few sentences:

> Gaddum: "One logical consequence of the adoption of this method (i.e. transforming into a logarithmic scale S.Ď.) would be that the mean of the logarithms or the geometrical mean (more exactly: the logarithm of the geometrical mean S.Ď.) of the observations would be taken as the most likely value (more exactly: as the logarithm of the most likely value S.Ď.) instead of the arithmetic mean."

This opinion of Gaddum is adopted by Hancock (1948a) who even starting from that basis recommends the use of the geometric mean as a mean value in evaluating the stock in a deposit (1948b).

In opposition, Dunkin (1948) reproaches Hancock for not having given any logical reason, justifying the preference of the geometric mean to the arithmetic mean in calculating the stock of a deposit. In his reply Hancock (1948b) tried to prove concretely that his assertion on the geometric mean is correct. In one part he defends Gaddum's assertion and insists that no defence or proof need be given of its correctness, for common sense and deduction on the part of the reader is sufficient; further he tries to deduce that if in a normal distribution the arithmetic mean is said to be the most likely value, then even in case of some abnormal distribution, which may be converted into a normal distribution by means of elementary functions, the arithmetic mean of the converted values must comply with the most likely value of the original multitude of values.

Ahrens (1954) himself regards the mode as identical with the geometric mean, but without any discussion.

We shall now try to point out the main source of error incurred by the said authors in their considerations, namely neglecting the difference between continuous and discrete distributions. In the continuous distribution functions [as shown, e.g. in equations (1) and (5)] signify the so-called density of distribution of probabilities, i.e. the probability, that the given value ξ complies with the inequality

$$X \leqslant \xi < X + dx$$

and its values, have the dimensions of

$$\frac{\text{probability}}{\text{width of the interval}}$$

If we alter the width of a given interval by conversion, it is evident, that the respective density of distribution of probabilities will also have altered, since the number of values, lying in this interval, remains unchanged. From this we clearly see that a point on a curve representing the density of distribution of probabilities has not, in general the same qualities after conversion in another scale. Thus for example the maximum need not comply with the maximum and the like..... as we showed in the example of continuous lognormal distribution. One must also realize that in continuous distribution the probability is zero that any value of a given multitude should reach exactly a definite magnitude.

Quite different are the conditions in a discrete distribution. Thus we may find for every precisely defined value a certain probability and only outside these values does the probability equal zero. In this case the density of distribution of probabilities has no importance at all. Furthermore it is clear that the probability of finding the original value is the same as the probability of finding the converted value, so that the curves, showing the development of probabilities in both examples may be simply deduced from one another by converting the values on the abscissal axis. In such a case the points having the same numerical value of the abscissa, have the very same qualities, and accordingly coincides with maximum, the point of inflexion to the point of inflexion, etc.

Thus the supposition of that mode and geometric mean are equal in lognormal distribution, may be regarded as valid only in the case of discrete distribution. This evidently does not hold for any geological material whatever with respect to the concentration of the elements. This fact shows that there is no reason for leaving such a question to the discretion of the reader, to his deductive capacities, especially if he is not familiar with questions relating to the theory of probability.

From the preceeding considerations we may realize that there is no reason whatever to regard the geometric mean, or perhaps the most likely value of concentration as a representative value for the evaluation of a deposit. Supposing that the deposit was thoroughly sampled, the arithmetic mean is the only value reasonably founded (e.g. material balance).

References

Ahrens L. H. (1954) The lognormal distribution of the elements. *Geochim. et Cosmochim. Acta* **5,** 49–73; **6,** 121–131.

Dunkin H. H. (1948) Discussion of "Averaging reef samples". *Miner. Mag.* **79,** 152–153.

Ďurovič S. (1957) On the lognormal distribution of elements—I. *Geologicky sbornik SAV* **8,** 306–322.

Gaddum J. H. (1945) Lognormal distributions. *Nature, Lond.* **156,** 463–466.

Hald A. (1952) *Statistical Theory with Engineering Applications.* (Russ. Transl., Moscow) pp. 140–152. Wiley, New York.

Hancock R. T. (1948a) Averaging reef samples. *Miner. Mag.* **78,** 273–278.

Hancock R. T. (1948b) Reply to Dunkin's discussion of "Averaging reef samples". *Miner. Mag.* **79,** 219–221.

Miller R. L. and Goldberg E. D. (1955) The normal distribution in geochemistry. *Geochim. et Cosmochim. Acta* **8,** 53–62.

Geochimica et Cosmochimica Acta, 1959, Vol. 15, pp. 337 to 341. Pergamon Press Ltd. Printed in Northern Ireland

Some reconnaissance observations on the combined use of ion-exchange enrichment and spectrochemical analysis for the determination of trace constituents in silicate rocks

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Abstract—A reconnaissance investigation has been made of the possible combined use of ion-exchange enrichment (cation and anion) and spectrochemical analysis for the determination of several rare elements, notably Ag, Be, Bi, Cd, Cs, In, La, Mo, Nb, Sn, Pb, Tl, Y and Zn, in silicate rocks and allied materials. Observations which have been carried out on granite G-1, a specimen of Cape granite, and diabase W-1, indicate that many of these elements should be easily detected in a wide variety of rocks and soils. The scope of the combined procedure seems to be immense and it is evidently possible to determine several elements in a single operation; the combined procedure should be particularly useful for investigating the general geochemistry of Bi.

Introduction

Spectrochemical methods of analysis are perhaps the most widely used general procedures for determining trace elements in rocks, soils, minerals and meteorites. The advantages of spectrochemical methods are many (Taylor and Ahrens, in press; Ahrens, 1957), but it is nevertheless not possible to employ them for the determination of a large number of trace elements because their concentrations are below spectrochemical detection limit concentrations, and other methods must be used. Though the other methods may be most effective they are invariably specific and a thorough investigation of the composition of a rock, soil, mineral or meteorite involves a large number of lengthy separate analytical operations. There is clearly a place therefore for procedures which are more sensitive than the usual spectrochemical methods of direct excitation of sample powders and which are comparatively rapid and applicable to many elements.

If the concentration of an element is very low it is often necessary to enrich it before a determination can be carried out by one of the several general procedures, spectrography, polarography, or colorimetry, for example. Many enrichment procedures are chemical and specific for one or a small number of elements; several have been used in conjunction with the spectrograph, for example by Mitchell and co-workers (Mitchell, 1957: several elements in plants and soils), Liebenberg (1956: Cs in rocks), and Berman (1957: La, Ce, Nd, Yb and Y in granite G-1 and diabase W-1). Apart from the fact that many enrichment procedures are restricted, chemistry may be complex and errors can arise from absorption and occlusion. A simple versatile enrichment procedure which involves a minimum number of chemical operations would offer most advantages and in this respect the use of an ion-exchange procedure seems a likely possibility.

In our present paper we wish to discuss the combined use of ion-exchange procedures (anion and cation) and spectrochemical analysis. We have prepared this brief and preliminary account because although many of the investigations

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are still in their reconnaissance stage they have revealed so clearly the potential value of the combined procedure: it will be our main purpose to illustrate the general principles of the procedure and its scope in geochemistry and cosmochemistry; details of analytical methods will be given elsewhere.

Our investigations have been carried out mainly on the standard rocks G-1 and W-1 (for recent review of data, see Ahrens and Fleischer, in press), a sample of Cape granite kindly provided by Prof. E. S. W. Simpson (Department of Geology, University of Cape Town) and a specimen of Limerick chondrite.

Discussion

(1) *Elements which have been investigated*

The investigations so far have been concerned mainly with several elements whose concentrations in igneous rocks and soils lie either in the neighbourhood of their spectrochemical detection limits or somewhat lower than these limits: we

Table 1. Estimated crustal abundances and approximate spectrochemical detection limits (d.c. arc) of some rare elements

Elements	Abundance (p.p.m.)	Detection limit (p.p.m.)	Remarks
Ag	0·1	0·5	Virtually never
Be	2	10	Very uncommon
Bi	0·2	20	Never
Cd	0·15	10	Never
Cs	6	2	Sometimes in granite
In	0·11	1	Never
La	18	10	Sometimes
Mo	1	5	Fairly common
Nb	24	30	Never
Nd	24	10	Rare
Pb	15	5	Sometimes in granite
Sn	40	10	Sometimes in granite
Tl	1·3	1	Occasionally in granite
Y	28	10	Sometimes
Zn	110	100	Occasionally in ferro magnesians

have not investigated extremely rare elements such as Re and noble metals such as Pt, Pd, Os, etc. Table 1 lists these elements together with their estimated crustal abundances (Rankama, 1954, among other sources) and their approximate detection limit concentrations in the d.c. arc (Ahrens, 1951). The remarks in the appropriate column in Table 1 have been inserted to provide an indication as to whether or not an element is likely to be detected by direct spectrochemical excitation in common rock types such as granite and basalt. Most of the elements listed in Table 1 are either only occasionally detected or never at all.

Before turning to discuss the combined procedure we shall mention one specialised fairly general spectrochemical procedure, the so-called double-arc. It is highly sensitive for several of the spectrochemically volatile elements, notably Tl,

In, Zn and Pb, and has been used for their determination (Shaw *et al.*, 1950; Shaw 1952a,b; Wedepohl, 1953, 1956).

2. *Principles of the combined procedure*

The principles of ion exchange have been described in several texts (Samuelson, 1953 and Kitchener, 1957, for example). For the purpose here we shall briefly recall a few relevant points. Ion exchange resins are of two types, cation resins and anion resins. Each has been investigated for the purpose at hand; we shall consider first cation exchange chromatography with HCl elution. When a solution containing several cations and anionic complexes (e.g. $SnCl_6^{2-}$) is adsorbed on a cation resin and eluted with HCl, most of the anionic complexes pass through the column first followed by the cations. The order in which the cations appear in the eluate is usually M^+ cations, M^{2+} cations, and finally M^{3+} cations. Within each charge group the order is usually according to size, cations with smaller radius moving through more rapidly than those with a large radius; for example, in the alkali metals the order is Li^+, Na^+, K^+, Rb^+ and Cs^+. Irregularities can occur and certain cations of given charge may appear in the same volume eluate as others of different charge. An element may be separated or obtained in a highly concentrated form (see, e.g., Pinson, 1953; Schumacher, 1956; Aldrich *et al.*, 1953), by careful control of the column conditions but for our purpose it is necessary only to concentrate the element to within the detection limit concentration of the spectrograph. In most d.c. arc spectrochemical procedures, up to about 100 mg of powder may be accommodated into the electrode; accordingly, on the basis of 1 g of original sample, an increase in sensitivity by a factor of about ten may be anticipated provided the total quantity of trace metal can be concentrated into a volume of eluate which yields up to 100 mg or so of residue. Greater sensitivity may be achieved by using a larger sample.

In our experiments, the powdered sample is treated with HF and $HClO_4$ and taken to dryness; the residue is taken up in a minimum volume of HCl and poured on to Dowex 50 resins (8×, 200–400 mesh) in the hydrogen form. Elutions with 1, 2, 2·5, 3 and 6 N HCl have been made. For monitoring purposes 20–30 ml fractions were collected on an automatic fraction collector, taken to dryness and arced to completion at 3A. The spectrograph is useful in this respect because the spectrum of each fraction provides a fairly complete and permanent record of its composition. These experiments showed that, apart from some irregularities and surprises (Edge and Ahrens, in preparation), the sequence in which elements moved through the column accorded with that anticipated from various papers in the literature. This sequence is given as the first horizontal column in Table 2.

For the purposes of analysis, rather than of monitoring, several of the comparatively small fractions may be consolidated into a large volume fraction, according to the principal constituent which happens to be present, as indicated by the second horizontal column in Table 2. Figure 1 shows spectra of the residues from some of these eluate fractions which have been obtained from a gram of granite G-1; the sharp change in composition is clear.

Many elements form chloro-complexes in concentrated or fairly concentrated

HCl and when a solution of chlorides is passed through an anion exchange column, the anionic chloro-complexes are held on the column whereas the cations appear in the eluate. Several of the 18-electron elements such as Ag, Cu, Au, Cd, Zn, Tl, Bi and Pb, together with a few others including Fe^{III}, form stable chloro-complexes. These elements may be removed from the column by destroying the complex: either by eluting with dilute HCl, dilute HNO_3 or dilute H_2SO_4, and in this way a fraction concentrated in the above elements may be obtained. Figure 2 shows the results of an experiment which has been carried out on the anion resin.

Table 2

Pt	Sn	Ti	Fe	Na	K	Rb	Cs	Ca	Sr	Ba	RE_s
	Ti		Fe	Na	K				Ca		

A 10 g sample of Cape granite was decomposed with HF and dried. The residue was taken up in HCl and passed through a column packed with Amberlite IR 400 (Cl form); this was eluted with HNO_3 and Fig. 2 shows the spectrum of the residue of the 50–500 ml eluate fraction. Many lines of the heavy metals Pb, Bi, Tl, Zn, Cd (barely detectable) and Ag appear. Several of the lines are very intense indeed. Direct excitation of the Cape granite powder showed only very weak Pb 4057 and no sign of the other elements. A similar experiment on diabase W-1 revealed detectable Bi, Tl, Ag, Pb and Zn.

The concentration of an element in a fraction is determined spectrochemically with the aid of appropriate synthetic standards and on the assumption that recovery is complete, it is possible to obtain a quantitative estimate of the element in the original rock, soil or meteorite sample itself.

Some conclusions on the apparent scope of the combined procedures

It will not be possible to demonstrate fully the scope of the combined procedures in geochemistry until they have been thoroughly tested on a wide variety of rocks, minerals, soils and meteorites. Nevertheless, the reconnaissance investigations on G-1, W-1, the Cape granite and a meteorite lead to the conclusion that the scope should be wide and the application useful; they indicate clearly that provided 5–10 g of sample are taken, most of the rare elements listed in Table 1 will be determinable in a large variety of igneous, metamorphic and sedimentary rocks and many meteorites and, of considerable significance, that several of the elements may be determined in a single analytical operation. For certain of these elements the combined procedures should be invaluable for obtaining general basic geochemical data: Bi is perhaps the best example, as virtually no data on its abundance in common rocks and soils are known.

References

Ahrens L. H. (1951) *Wavelength Tables of Sensitive Lines.* Addison–Wesley, Brookline, Mass.

Ahrens L. H. (1957) The spectrograph in geochemistry and cosmochemistry. *Soil Science* **83,** 33.

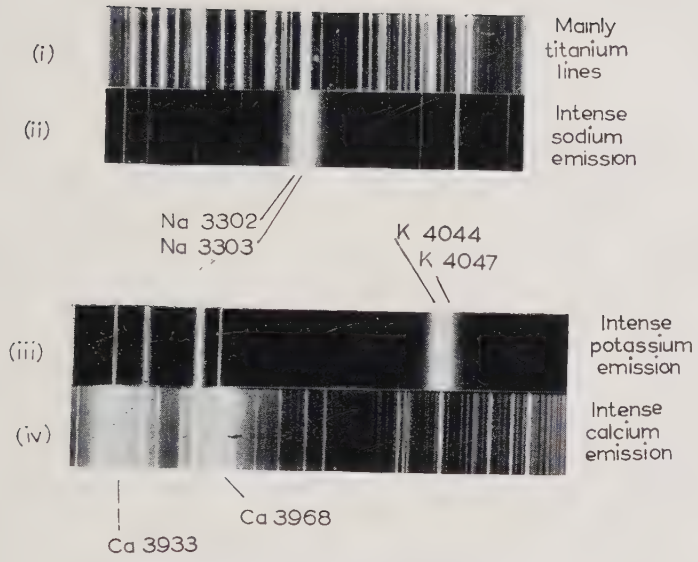

Fig. 1. Arc spectra (over two wavelength ranges) of residues from successive eluate fractions; cation column. Granite G–1.

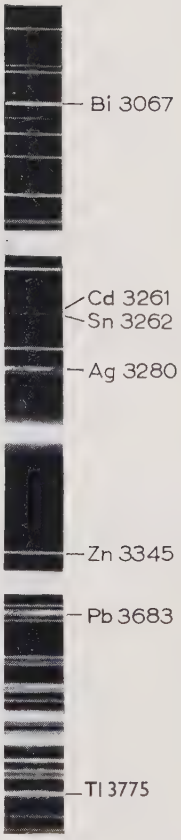

Fig. 2. Arc spectrum of residue from 50–500 ml eluate fraction (HNO_3); anion column. Residue mixed with 20 mg NaCl to clear CN emission and provide bulk. Cape Granite. Note particularly the presence of Bi 3067 and the high intensity of Tl 3775.

Ahrens L. H. and Fleischer M. Report on trace constituents in standard granite G-1 and standard diabase W-1. *U.S. Geol. Surv. Bull.* In press.

Aldrich L. T., Doak J. R. and Davis G. L. (1953) The use of ion exchange column in mineral analysis for age determination. *Amer. J. Sci.* **251,** 377.

Berman S. (1957) Determination of Y, La, Ce, Nd and Yb in test samples granite G-1 and diabase W-1 by a combined chemical spectrographical technique. *Geochim. et Cosmochim. Acta* **12,** 271.

Edge R. A. and Ahrens L. H. In preparation.

Kitchener J. A. (1957) *Ion-exchange Resins.* Methuen, London.

Liebenberg C. J. (1956) The spectrochemical determination of Cs in igneous rocks using a chemical concentration procedure. *Geochim. et Cosmochim. Acta* **10,** 196.

Mitchell R. L. (1957) Spectrochemical methods in soil investigations. *Soil Sci.* **83,** 1.

Pinson W. H. (1953) *Ann. Prog. Report,* Dept. of Geology and Geophysics, Mass. Inst. Technology.

Rankama K. (1954) *Isotope Geology.* Pergamon Press, London.

Samuelson, —. (1953) *Ion Exchangers in Analytical Chemistry.* Wiley, New York.

Schumacher E. (1956) Isolierung von K, Rb, Sr, Ba und Seltenen Erden aus Steinmeteoriten. *Helv. Chim. Acta* **39,** 531.

Shaw D. M. (1952a) The geochemistry of indium. *Geochim. et Cosmochim. Acta* **2,** 185.

Shaw D. M. (1952b) The geochemistry of thallium. *Geochim. et Cosmochim. Acta* **2,** 118.

Shaw D. M., Joensuu O. I. and Ahrens L. H. (1950) A soluble-arc method for spectrochemical analysis of geological materials. *Spectrochim. Acta* **4,** 233.

Taylor S. R. and Ahrens L. H. Spectrochemical Analysis. *Physical and Chemical Methods in Geochemistry.* (Edited by Smales and Wager). Interscience, New York. In preparation.

Wedepohl K. H. (1953) Untersuchung zur Geochemie des Zincums. *Geochim. et Cosmochim. Acta* **3,** 93.

Wedepohl K. H. (1956) Untersuchung zur Geochemie des Bleis. *Geochim. et Cosmochim. Acta* **10,** 69.

Geochimica et Cosmochimica Acta, 1959, Vol. 15, pp. 342 to 369. Pergamon Press Ltd. Printed in Northern Ireland

Data of rock analyses—V

Bibliography and index of rock analyses in the Australian periodical and serial literature*

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> . . . just as each of the American, English, German and French schools has an individuality of its own, so will authors in Australia and New Zealand surely leave the impress of their work on contemporary thought. Each is worthily doing his part in laying the foundation stones of the future edifice of the Australasian petrology.
>
> W. H. TWELVETREES

THE rock analysis data in the Australian periodical and serial literature published from 1914 to 1953 inclusive are presented in Part V, following the pattern set in Parts I–IV (listed on page 369). Eighty-one journals were examined, about thirty of which have continuous publication over the entire 40-year period. The bibliography contains 240 references taken from thirty-five journals, with the number of analyses and the rock types in each reference indicated. In the Australian literature, as in that of Africa and New Zealand, we are dealing with a regional literature in that only occasional analyses of rocks from outside the country are published in the journals. The geographic index shows the distribution of the 968 analysed rocks, by states and areas within Australia, and in Antarctica, New Guinea and the New Hebrides Islands, the only areas outside of Australia represented. The rock-name index, adhering strictly to the names designated by the authors, refers to the bibliographic references. Porphyries (and porphyrites) and xenoliths are double listed, both as groups and under individual descriptive names.

A few remarks about the selection of analyses are in order here. Altogether, 968 analyses of igneous rocks, metamorphic rocks and meteorites have been selected, and as far as it is possible to determine these are new analyses, previously unpublished. However, because many analyses of Australian rocks have been published in British journals, duplication may occur which would be impossible to detect until an exhaustive search of the British literature had been completed. The collection of analyses of Western Australian rocks published by E. S. Simpson in 1916 contains seventy-seven analyses that we think have not been published elsewhere and these are included here. Our selection also shows a rather liberal inclusion of the altered rocks that were analysed as part of the early investigations of the Western Australian mining fields.

It is a personal pleasure to thank Dr. GERMAINE A. JOPLIN and many of her colleagues, and Dr. GEORGE T. FAUST, who have generously contributed time, knowledge and pertinent suggestions, all of which have resulted in a better manuscript.

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Periodical and Serial Literature

AUSTRALIA (General)

Aerial, Geological and Geophysical Survey of Northern Australia, Report (Northern Territory) (1936–).
——, Report (Queensland) (1936–).
——, Report (Western Australia) (1935–).
Australasian Association for the Advancement of Science, Report (1888–1929). See Australian and New Zealand Association for the Advancement of Science, Report.
Australasian Institute of Mining Engineers, Proceedings (1897 -1919). See Australasian Institute of Mining and Metallurgy, Proceedings.
——, Transactions (1893–1912).
Australasian Institute of Mining and Metallurgy, Proceedings (1919–). Formerly Australasian Institute of Mining Engineers, Proceedings.
Australia, Commonwealth Scientific and Industrial Research Organization, Bulletin (1917–). Name may vary; see Commonwealth of Australia, Advisory Council of Science and Industry, Bulletin.
Australia Mineral Resources Survey, Summary Report (1945–).
Australian and New Zealand Association for the Advancement of Science, Report (1931–). Formerly Australasian Association for the Advancement of Science, Report.
Australian Journal of Science (1938–).
Australian Mining and Engineering Review (1908–1910). See Mining and Engineering Review.
Australian Science Abstracts (1922–).
Chemical Engineering and Mining Review (1917–). Formerly Mining and Engineering Review.
Commonwealth of Australia, Advisory Council of Science and Industry, Bulletin. (1917–). Name may vary; see Australia, Commonwealth Scientific and Industrial Research Organization, Bulletin.
——, Bureau of Mineral Resources, Geology and Geophysics, Bulletin (1932–).
——, Pamphlet (1943–).
——, Report (1948–).
Geological Society of Australia, Journal (1954–).
——, News Bulletin (1953–1956).
Great Barrier Reef Committee, Report (1925–).
Institution of Engineers, Australia, Journal (1929 -).
Mining and Engineering Review (1911–1917). Formerly Australian Mining and Engineering Review. See Chemical Engineering and Mining Review.
New Guinea Territory, Geological Bulletin (1939–).
Territory of Papua, Bulletin (1913–1921).

NEW SOUTH WALES

Australian Museum, Memoir (1851–).
——, Miscellaneous Publications (1884–1916).
——, Records (1890–).
Linnean Society of New South Wales, Proceedings (1876–).
New South Wales Department of Mines, Annual Report (1876–).
New South Wales Geological Survey, Bulletin (1922–1925).
——, Geological Reports. Special volume of New South Wales Department of Mines, Annual Report 1939–1945.
——, Memoirs (1887–).
——, Mineral Resources (1898–).
——, Records (1889–1922).
Royal Society of New South Wales, Journal and Proceedings (1866–).
——, Monograph (1950–).

QUEENSLAND

Queensland Geological Survey, Bulletin (1895–1902).
——, Publication (1879–).
——, Records (1904–1911).
Queensland Government Mining Journal (1900–).
Queensland Museum, Annals (1891–1911).
——, Memoirs (1912–).
Queensland Naturalist (1908–).
Queensland Under Secretary for Mines, Annual Report (1880–).
Royal Society of Queensland, Proceedings (1885–).
University of Queensland, Department of Geology, Papers (1937–). Both reprinted and original papers.

SOUTH AUSTRALIA

Royal Society of South Australia, Memoirs (1899–1913).
——, Transactions (1877–).
South Australia Department of Mines, Mining Review (1918–). Formerly South Australia, Review of Mining Operations.
South Australia Geological Survey, Bulletin (1912–).
——, Report (1912–1916).
South Australia, Review of Mining Operations (1904–1917). See South Australia Department of Mines, Mining Review.
South Australian Museum, Records (1918–).
South Australian Naturalist (1919–).

TASMANIA

Queen Victoria Museum, Records (1942–).
Royal Society of Tasmania, Papers and Proceedings (1849–).
Tasmania Department of Mines, Geological Survey Record (1913–).
——, Underground Water Supply Paper (1921–).
Tasmania Geological Survey, Bulletin (1907–).
— , Mineral Resources (1915–).
, Report (1910–).
Tasmania, Report of the Director of Mines (1940–). Formerly Report of the Secretary for Mines.
——, Report of the Secretary for Mines (1883–1939). See Report of the Director of Mines.

VICTORIA

Mining and Geological Journal (1937–).
National Museum, Melbourne, Memoir (1906–).
Royal Society of Victoria, Proceedings (1859–).
Victoria Department of Mines, Annual Report of the Secretary for Mines (1889–).
Victoria Geological Survey, Bulletin (1903–).
– , Memoir (1903–).
— , Records (1902–).
Victorian Naturalist (1884–).
University of Melbourne, Collected Papers from the Science Laboratories (1910–). Reprints from other periodicals.

WESTERN AUSTRALIA

Royal Society of Western Australia, Journal and Proceedings (1914–). Formerly Western Australia Natural History and Science Society, Journal.
Western Australia Department of Mines, Bulletin (1945–).
, Report (1894–).

Western Australia Geological Survey, Annual Progress Report (1897–1939). See under Report.
——, Bulletin (1898–).
——, Memoir (1919–).
——, Report (1940–). Formerly Annual Progress Report.
Western Australia Natural History and Science Society, Journal (1904–1914). See Royal Society of Western Australia, Journal and Proceedings.

Bibliography

Alderman, Arthur R. (1927) Petrographic notes on tonalite from the Palmer district and biotite–norite from South Black Hill: Roy. Soc. S. Australia Tr. **51,** 20–23. *S. Australia:* 2; tonalite, biotite–norite.

Alderman, Arthur R. (1929) Magmatic differentiation at Mannum, South Australia: Roy. Soc. S. Australia Tr. **53,** 249–257. *S. Australia:* 2; aplite, basic dike.

Alderman, Arthur R. (1931) Petrographic notes in some basic rocks from the Mount Barker and Woodside districts: Roy. Soc. S. Australia Tr. **55,** 163–167. *S. Australia:* 3; dolerite amphibolite.

Alderman, Arthur R. (1932) The Henbury (Central Australia) meteoric iron: S. Australian Mus. Rec. **4,** No. 4, 555–563. *Northern Territory:* 1 meteorite.

Alderman, Arthur R. (1936) The Carraweena, Yandama and Cartoonkana meteoric stones: S. Australian Mus. Rec. **5,** No. 4, 537–546. *S. Australia:* 1 meteorite; *New South Wales:* 1 meteorite.

Alderman, Arthur R. (1938) Augen-gneisses in the Humbug Scrub area, South Australia: Roy. Soc. S. Australia Tr. **62,** 168–181. *S. Australia:* 6; augen-gneiss, soda hybrid, gneiss, sericite schist.

Alderman, Arthur R. (1938) A siderolite from Pinnaroo, South Australia: Roy. Soc. S. Australia Tr. **64,** 109–113. *S. Australia:* 1 meteorite.

Anderson, Charles and John C. H. Mingaye (1913) Description and analysis of the Binda meteorite: Australian Mus. Rec. **10,** No. 5, 49–52. *New South Wales:* 1 meteorite.

Andrews, Ernest C. (1915) The Canbelego, Budgery and Budgerygar mines: New South Wales Geol. Surv., Min. Res. **18,** 121 pp. *New South Wales:* 3; phyllite, slate.

Andrews, Ernest C. (1916) The molybdenum industry in New South Wales: New South Wales Geol. Surv., Min. Res. **24,** 199 pp. *New South Wales:* 3; biotite granite, granite, muscovite granite.

Aurousseau, Marcel (1926) Analyses of three Australian rocks: Linnean Soc. New South Wales Proc. **51,** No. 208, 614–626. *New South Wales:* 1 granite; *Tasmania:* 1 nepheline basanite; *W. Australia:* 1 amphibolite.

Baker, George (1942) The heavy minerals of some Victorian granitic rocks: Roy. Soc. Victoria Proc. **54,** Pt. 2, 196–223. *Victoria:* 4; granodiorite.

Baker, George (1953) Natural sinters from Mt. Remarkable and Tempe Downs: Roy. Soc. S. Australia Tr. **76,** 27–33. *Northern Territory:* 1 sinter; *S. Australia:* 1 sinter.

Basnett, Elizabeth M. (1939) Studies in metamorphism and assimilation in the Wellington district, N.S.W. I. Hybridization in the Wuuluman Creek intrusion: Roy. Soc. New South Wales J. and Proc. **73,** Pt. 3, 161–189. *New South Wales:* 5; altered and hybridized dolerites, spotted hybrid rocks, keratophyre.

Basnett, Elizabeth M. (1942) Studies in metamorphism and assimilation in the Wellington district, N.S.W. II. The dynamic and contact metamorphism of a group of ultrabasic rocks: Roy. Soc. New South Wales J. and Proc. **76,** Pt. 1, 55–81. *New South Wales:* 6; spinel amphibolite, epidote amphibolite, feldspar-amphibolite, pennine-ferroantigorite-tremolite schist, antigorite-tremolite-talc schist, tremolite rock.

Benson, W. Noel (1915a) The geology and petrology of the Great Serpentine Belt of New South Wales. Part 4. The dolerites, spilites and keratophyres of the Nundle district: Linnean Soc. New South Wales Proc. **40,** No. 157, 121–173. *New South Wales:* 6; dolerite, quartz dolerite, variolite, keratophyre, magnetite keratophyre.

Benson, W. Noel (1915b) The geology and petrology of the Great Serpentine Belt of New South Wales. Part 5. The geology of the Tamworth district: Linnean Soc. New South Wales Proc. **40,** No. 159, 540–624. *New South Wales:* 3; labradorite dolerite, spilite, quartz keratophyre.

Benson, W. Noel (1918) The geology and petrology of the Great Serpentine Belt of New South Wales. Part. 7. The geology of the Loomberah district and a portion of the Goonoo Goonoo estate: Linnean Soc. New South Wales Proc. **43,** No. 170, 320–360, 363–384. *New South Wales:* 2 dolerite.

Blatchford, Torrington (1927) The geology of portions of the Kimberley Division, with special reference to the Fitzroy Basin and the possibilities of the occurrence of mineral oil: West Australia Geol. Surv. **93,** 56 pp. *W. Australia:* 1 leucitite.

Bowley, Harry (1923) Mineralogy, mineral technology and geochemistry. In Annual report of the Chemical Branch: West Australia Dept. Mines Rpt. 1922, 117–120. *W. Australia:* 2 quartzite.

Bowley, Harry (1926) Mineralogy, mineral technology and geochemistry. In Annual report of the Chemical Branch: West Australia Dept. Mines Rpt. 1925, 167–172. *W. Australia:* 2; quartz epidiorite, lamprophyre.

Bowley, Harry (1945) Annual report of the Government Mineralogist, Analyst and Chemist for the year 1944: West Australia Dept. Mines Rpt. 1944, 128–155. *W. Australia:* 4; dolerite gabbro, garnetized gabbro, serpentine.

Bowley, Harry (1948) Annual report of the Government Mineralogist, Analyst and Chemist for the year 1945: West Australia Dept. Mines Rpt. 1945, 1–31. *W. Australia:* 1 granite.

Broadhurst, Edward and J. D. Campbell (1933) The geology and petrology of the Mt. Leinster district, N. E. Victoria: Roy. Soc. Victoria Proc. **45,** Pt. 2, 219–240. *Victoria:* 3; soda syenite, granodiorite, granite porphyry.

Brown, Ida A. (1928) The geology of the south coast of New South Wales. Part I. The Palaeozoic geology of the Moruya district: Linnean Soc. New South Wales Proc. **53,** No. 217, 151–192. *New South Wales:* 10; biotite granite, granodiorite, quartz diorite, diorite gabbro, hornblende gabbro, aplite, hornblende-quartz-porphyrite, granite porphyry, basic inclusion.

Brown, Ida A. (1930) The geology of the south coast of New South Wales. Part 3. The monzonitic complex of the Mount Dromedary district: Linnean Soc. New South Wales Proc. **55,** No. 231, 637–698. *New South Wales:* 9; banatite, monzonite, olivine monzonite, shonkinite, covite, pyroxenite, kedabekite, melanite melteigite.

Brown, Ida A. (1931) The stratigraphical and structural geology of the Devonian rocks of the south coast of New South Wales: Linnean Soc. New South Wales Proc. **56,** No. 237, 461–496. *New South Wales:* 4; basalt, rhyolite.

Brown, Ida, A. (1933) The geology of the south coast of New South Wales, with special reference to the origin and relationships of the igneous rocks: Linnean Soc. New South Wales Proc. **58,** No. 249–250, 334–362. *New South Wales:* 2 basalt.

Browne, William R. (1920a) The geology and petrology of the Great Serpentine Belt of New South Wales. Part 9. The geology, palaeontology and petrography of the Currabubula district with notes on adjacent regions. Section C, Petrography: Linnean Soc. New South Wales Proc. **45,** No. 179, 405–423. *New South Wales:* 1 quartz keratophyre.

Browne, William R. (1920b) The igneous rocks of Encounter Bay, South Australia: Roy. Soc. S. Australia Tr. **44,** 1–57. *S. Australia:* 7; granite, aplite, soda aplite, quartz mica diorite, albite mica syenite, dolerite.

Browne, William R. (1922a) Report on the petrology of the Broken Hill region, excluding the Great Lode and its immediate vicinity, Appendix I. In the geology of the Broken Hill district: New South Wales Geol. Surv. Mem. **8,** 295–353. *New South Wales:* 24; gneiss, quartzite, augen-gneiss, platy gneiss, sillimanite gneiss, pegmatitic gneiss, sericite schist, quartz-feldspar-sericite schist, epidosite, cordierite aplite, barium-rich rock, garnet amphibolite, garnet-quartz-magnetite rock, dolerite (uralitic), hornblende gabbro, hornblende-hypersthene gabbro.

Browne, William R. and William A. Greig (1922b) On an olivine-bearing quartz-monzonite from Kiandra, N.S.W.: Roy. Soc. New South Wales J. and Proc. **56,** 260–277. *New South Wales:* 2; quartz monzonite, monzonite porphyry.

Browne, William R. and Harold P. White (1927) The hypersthene andesite of Blair Duguid, near Allandale, N.S. Wales: Roy. Soc. New South Wales J. and Proc. **60,** 372–387. *New South Wales:* 2 hypersthene andesite.

Browne, William R. and Harold P. White (1929) Alkalization and other deuteric phenomena in the Saddleback trachybasalt at Port Kembla: Roy Soc. New South Wales J. and Proc. **62,** 303–340. *New South Wales:* 2; trachybasalt, dark intrusive.

Bryan, Walter H. (1923) Geology and petrology of the Enoggera granite and the allied intrusives: Roy. Soc. Queensland Proc. **34,** 123–160. *Queensland:* 1 quartz mica diorite.

Chalmers, R. Oliver (1941) The petrology of the Five Islands, Port Kembla, New South Wales: Australian Mus. Rec. **21,** No. 1, 27–42. *New South Wales:* 1 acid latite.

Chemical Staff, Broken Hill Mines (1922) Analyses of rocks and minerals of Broken Hill district, Appendix III. *In* The geology of the Broken Hill district: Geol. Surv. New South Wales Mem. **8,** 397–402. *New South Wales:* 19; sericite schist, garnet-sillimanite-cordierite-schist, quartzite, granulite, augen-gneiss, amphibolite, quartz notire, zoisite epidosite, garnet sandstone, epidiorite. Ten of the analyses appearing in this appendix are duplicates run on specimens listed under Browne (1922a) and Stillwell (1922).

Clarke, Edward de C. (1914) Notes on the geology and mining at Sandstone and Hancock's, East Murchison goldfield: W. Australia Geol. Surv. B. **62,** 66 pp. *W. Australia:* 4; chlorite schist, graphite schist.

Clarke, Edward de C. (1925) The field geology and broader mining features of the Leonora-Duketon district: West Australia Geol. Surv. B. **84,** 66 pp. *W. Australia:* 1 andalusite quartz schist.

Clarke, Edward de C. and F. A. Williams (1927) The geology and physiography of parts of the Darling Range near Perth: Roy. Soc. W. Australia J. and Proc. **12,** 161–178. *W. Australia:* 5 epidorite.

Cochrane, Gregory W. and H. R. Samson (1950) The geology of the Nowa Nowa-South Buchan area, Victoria: Roy. Soc. Victoria Proc. **60,** 93–122. *Victoria:* 2; quartz syenite, quartz andesite.

Colditz, Margaret J. (1948) The petrology of the Silurian volcanic sequence at Wellington, N.S.W.: Roy. Soc. New South Wales J. and Proc. **81,** Pt. 3, 180–197. *New South Wales:* 5; basalt, augite-hornblende-andesite, hornblende trachyandesite, augite porphyrite, augite andesite.

Cook, G. A. (1916) Notes on the geology of the Coburg area: Roy. Soc. Victoria Proc. **28,** Pt. 2, 173–182. *Victoria:* 1 basalt.

David, T. W. Edgeworth, Herbert S. Summers and Gustav A. Ampt (1927) The Tasmanian tektite—Darwin glass: Roy. Soc. Victoria Proc. **39,** Pt. 2, 167–190. *Tasmania:* 2 Darwin glass.

Davis, C. E. S. (1943) The geology and physiography of the Gosnells area: Roy. Soc. W. Australia J. **27,** 245–264. *W. Australia:* 2 granite.

Dunn, E. J. (1914a) The Golden Bar and Golden Bar Extended mines, Chiltern: Victoria Geol. Surv. Rec. **3,** Pt. 3, 277–278. *Victoria:* 1 dike.

Dunn, E. J. (1914b) Further notes on australites: Victoria Geol. Surv. Rec. **3,** Pt. 3, 322–326. *Victoria:* 2; obsidian, tachylite.

Edwards, Austin B. (1932a) The geology and petrology of the Black Spur area (Healesville): Roy. Soc. Victoria Proc. **44,** Pt. 1, 49–76. *Victoria:* 3; quartz dacite, β-quartz-hypersthene-biotite dacite, hypersthene dacite.

Edwards, Austin B. (1932b) The geology and petrology of the Warburton area, Victoria: Roy. Soc. Victoria Proc. **44,** Pt. 2, 163–181. *Victoria:* 4; soda rhyolite, α-quartz biotite dacite, feldspar hornblende porphyrite, granodiorite.

Edwards, Austin B. (1934) Tertiary dykes and volcanic necks of South Gippsland, Victoria: Roy. Soc. Victoria Proc. **47,** Pt. 1, 112–132. *Victoria:* 8; olivine nephelinite, olivine basalt, olivine analcite dolerite, monchiquite, monchiquite basalt.

Edwards, Austin B. (1936) Tholeiite basalts from Cape Gosselin, Western Australia: Roy. Soc. W. Australia J. **22,** 19–23. *W. Australia:* 1 tholeiite.

Edwards, Austin B. and John G. Easton (1937a) The igneous rocks of north-eastern Benambra: Roy. Soc. Victoria Proc. **50,** Pt. 1, 69–96. *Victoria:* 9; granite, biotite granite, rhyolite, porphyry, quartz porphyry, quartz feldspar porphyrite, labradorite porphyrite, quartz augite diorite.

Edwards, Austin B. (1937b) Quartz-diorite magma in eastern Victoria: Roy Soc. Victoria Proc. **50,** Pt. 1, 97–109. *Victoria:* 2; hypersthene dacite, inclusion.

Edwards, Austin B. (1938) Tertiary tholeiite magma in Western Australia: Roy. Soc. W. Australia J. **24,** 1–12. *W. Australia:* 2 tholeiite.

Edwards, Austin B. and W. Crawford (1940) The Cainozoic volcanic rocks of the Gisborne district, Victoria: Roy. Soc. Victoria Proc. **52,** Pt. 2, 281–311. *Victoria:* 1 ; hypersthene trachyandesite, hypersthene basalt, hypersthene gabbro, hypersthene augite olivine basalt, olivine basalt, olivine augite basalt, iddingsite basalt, limburgite.

Edwards, Austin B. and Edward de C. Clarke (1941a) Some Cambrian basalts from the East Kimberley, Western Australia: Roy. Soc. W. Australia J. **26,** 77–94. *W. Australia* 6; basalt, quartz basalt, feldspar basalt, olivine basalt.

Edwards, Austin B. (1941b) The crinanite laccolith of Circular Head, Tasmania: Roy. Soc. Victoria Proc. **53,** Pt. 2, 403–415. *Tasmania:* 5 crinanite.

Edwards, Austin B. and George Baker (1942) The Pakenham meteorite: Roy. Soc. Victoria Proc. **54,** Pt. 1, 7–16. *Victoria:* 1 meteorite.

Edwards, Austin B. (1943) Some basalts from the North Kimberley, Western Australia: Roy. Soc. W. Australia J. **27,** 79–93. *W. Australia:* 2; two-pyroxene quartz dolerite, hornblende andesine basalt.

Edwards, Austin B. and George Baker (1944a) The Cranbourne meteorites: Natl. Mus., Melbourne, Mem. **14,** 23–35. *Victoria:* 4 meteorites.

Edwards, Austin B. and George Baker (1944b) Contact phenomena in the Morang Hills, Victoria: Roy. Soc. Victoria Proc. **56,** Pt. 1, 19–34. *Victoria:* 1 granodiorite.

Edwards, Austin B. (1946) The Moorumbunna meteorite: Roy. Soc. S. Australia Tr. **70,** 348–353. *S. Australia:* 1 meteorite.

Edwards, Austin B. (1947) Alkali hybrid rocks of Port Cygnet, Tasmania: Roy. Soc. Victoria Proc. **58,** Pts. 1–2, 81–115. *Tasmania:* 17; syenite porphyry, hauyne-sanidine-garnet-porphyry, sanidine tinguaite, tinguaite, syenite pegmatite, garnet orthoclasite, dolerite, uralitized dolerite, metamorphosed dolerite, leucocratic and melanocratic hybrid rocks.

Edwards, Austin B. (1950) The petrology of the Cainozoic basaltic rocks of Tasmania: Roy. Soc. Victoria Proc. **62,** Pt. 1, 97–120. *Tasmania:* 11; olivine basalt, olivine titanaugite basalt, iddingsite oligoclase basalt, limburgite, olivine nephelinite.

Edwards, Austin B. (1953a) The Wedderburn meteoritic iron: Roy. Soc. Victoria Proc. **64,** Pt. 2, 73–76. *Victoria:* 1 meteorite.

Edwards, Austin B. and Martin F. Glaessner (1953b) Mesozoic and Tertiary sediments from the Wahgi Valley, New Guinea: Roy. Soc. Victoria Proc. **64,** Pt. 2, 93–112. *New Guinea:* 2; tuffaceous greywacke; zeolitic andesitic tuff.

Edwards, Austin B. (1953c) Crinanite-picrite intrusions in the Nebo district of New South Wales: Roy. Soc. Victoria Proc. **65,** Pt. 1, 9–29. *New South Wales:* 15; crinanite, picrite, analcite-olivine dolerite, analcite-olivine-titanaugite dolerite, teschenite, titanaugite dolerite, titanaugite basalt, picritic rock.

England, H. N. (1935) Petrographic notes on intrusions of the Houghton magma in the Mount Lofty Ranges: Roy. Soc. S. Australia Tr. **59,** 1–15. *S. Australia:* 10; syenite, diorite, dolerite, quartz diorite.

Farquharson, Robert A. (1914a) Petrological observations on the rocks from Ora Banda. *In* The mining geology of Ora Banda, Broad Arrow goldfield: W. Australia Geol. Surv. B. **54,** 109–131. *W. Australia:* 2; zoisitized dolerite, epidiorite.

Farquharson, Robert A. (1914b) Petrography of the area. *In* The geology of the country between Kalgoorlie and Coolgardie: W. Australia Geol. Surv. B. **56,** 52–76. *W. Australia:* 4; quartz porphyry, soda porphyrite, tourmaline rock.

Farquharson, Robert A. (1916) Petrology. *In* The geology and ore-deposits of Meekatharra, Murchison goldfield: W. Australia Geol. Surv. B. **68,** 206–287. *W. Australia:* 5; albite, albite porphyry, chlorite slate, sericite phyllite, schist.

Farquharson, Robert A. (1917) The petrology of Westonia, with notes on rocks from Bullfinch, Golden Valley, Hatter's Hill and the Corinthian mine. *In* The geology and mineral resources of the Yilgarn goldfield. Part III. The gold belt north of Southern Cross including Westonia: W. Australia Geol. Surv. B. **71,** 263–312. *W. Australia:* 3; hornblende-quartz-feldspar-biotite gneiss, epidiorite, chlorite-quartz schist.

Feldtmann, Francis R. (1916) Contributions to the study of the geology and ore deposits of Kalgoorlie, East Coolgardie goldfield. Part III. W. Australia Geol. Surv. B. **69,** 152 pp. *W. Australia:* 9; amphibolite, greenstone, fuchsite-quartz-carbonate rock, graphitic schist, albite porphyrite quartz-dolerite greenstone, quartz-dolerite-tourmaline greenstone, talc mesitite.

Feldtmann, Francis R. (1921) The mining centres of Quinn's and Jasper Hill, Murchison goldfield: W. Australia Geol. Surv. B. **80,** 82 pp. *W. Australia:* 2 chlorite-quartz schist.

Feldtmann, Francis R. (1935) The Larkinville gold-mining centre, Coolgardie goldfield: W. Australia Geol. Surv. Ann. Prog. Rpt. 1934, 13–26. *W. Australia:* 2; graphitic rock, fuchsite-quartz rock.

Fenner, Charles (1940) Australites. Part IV. The John Kennett collection with notes on Darwin glass, bediasites, etc.: Roy. Soc. S. Australia Tr. **64,** 305–324. *S. Australia:* 2 silica glass.

Finucane, Kevin J. (1935) Mathinna and Tower Hill goldfields: Tasmania Geol. Surv. B. **43,** 128 pp. *Tasmania:* 1 carbonated dike rock.

Finucane, Kevin J. (1939) The blue asbestos deposits of the Hamersley Ranges, Western Australia: Aerial, Geol. and Geophys. Surv. N. Australia Rpt. **49,** 15 pp. *W. Australia:* 1 riebeckite rock.

Gaskin, Arthur J. (1944) Kaolinized granodiorite in the Bulla–Broadmeadows area: Roy. Soc. Victoria Proc. **56,** Pt. 1, 1–18. *Victoria:* 1 granodiorite (kaolinized).

Goode, B. F. (1927) The Mannum granite: Roy. Soc. S. Australia Tr. **51,** 126–128. *S. Australia:* 1 granite.

Grace, J. N. A. (1948) Mineralogy, mineral technology and geochemistry division, Annual report for the year ended 31st December, 1946: W. Australia Dept. Mines Rpt. 1946, 138–144. *W. Australia:* 1 dolerite.

Hanlon, Frederick N. (1945) The bauxites of New South Wales. Their distribution, composition and probable origin: Roy. Soc. New South Wales J. **78,** Pt. 3, 94–112. *New South Wales:* 2 basalt.

Harvey, Madeleine H. and Germaine A. Joplin (1941) A note on some leucite-bearing rocks from N.S.W., with special reference to an ultrabasic occurrence at Murrumburrah: Roy. Soc. New South Wales J. and Proc. **74,** Pt. 4, 419–442. *New South Wales.* 3; monchiquite, biotite-rich monchiquite, biotite-free monchiquite.

Hayton, J. D. (1950) An unusual rock type from the "Iron King" mine, Norseman: Appendix I. *In* Report of the Director of Government Chemical Laboratories for the year 1947: W. Australia Dept. Mines Rpt. 1947 24–25. *W. Australia:* 1 phlogopite-olivine rock.

Hills, E. Sherbon (1929) The geology and palaeontography of the Cathedral Range and Blue Hills, in north-western Gippsland: Roy. Soc. Victoria Proc. **41,** Pt. 2, 176–201. *Victoria:* 2; cordierite nevadite, rhyolite.

Hodge-Smith, Thomas (1924) Notes on the occurrences of zeolites, Ardglen, New South Wales: Australian Mus. Rec. **14,** No. 3, 213–222. *New South Wales:* 1 basalt.

Hodge-Smith, Thomas and Harold P. White (1926) The "Tieraco Creek" siderite: Australian Mus. Rec. **15,** No. 1, 66–68. *W. Australia:* 1 meteorite.

Hodge-Smith, Thomas (1929) The Elsinora meteorite, a new chondrite from New South Wales: Australian Mus. Rec. **17,** No. 1, 50–52. *New South Wales:* 1 meteorite.

Hodge-Smith, Thomas (1931) The Narellan meteorite, a new chondrite from New SouthWales: Australian Mus. Rec. **18,** No. 5, 283–285. *New South Wales:* 1 meteorite.

Hodge-Smith, Thomas (1932) The Weekeroo meteorite, a siderite from South Australia: Australian Mus. Rec. **18,** No. 6, 312–313. *South Australia:* 1 meteorite.

Hodge-Smith, Thomas (1937) An unrecorded meteorite from Coolac, New South Wales: Australian Mus. Rec. **20,** No. 2, 130–132. *New South Wales:* 1 meteorite.

Hodge-Smith, Thomas and Austin B. Edwards (1941) The Tawallah Valley meteorite: Australian Mus. Rec. **21,** No. 1, 1–8. *Northern Territory:* 1 meteorite.

Hodge-Smith, Thomas and R. Oliver Chalmers (1942) The Moorleah meteorite: Queen Victoria Mus. Rec. **1,** No. 1, 13–16. *Tasmania:* 1 meteorite.

Hossfeld, Paul S. (1925) The Tanunda Creek granite and its field relations: Roy. Soc. S. Australia Tr. **49,** 191–197. *S. Australia:* 1 granite.

Howard, Peter F. (1951) The basic igneous rocks of the Blinman dome: Roy. Soc. S. Australia Tr. **74,** Pt. 2, 165–188. *S. Australia.:* 1 dolerite.

Jack, R. Lockhart (1914) The geology of the County of Jervois, and of portions of the Counties of Buxton and York, with special reference to underground water supplies: S. Australia Geol. Surv. B. **3,** 47 pp. *S. Australia:* 7; granite, albitite, augen-gneiss.

Jack, R. Lockhart (1917) The geology of the Moonta and Wallaroo mining district: S. Australia Geol. Surv. B. **6,** 135 pp. *S. Australia:* 4; feldspar porphyry, schistose felsite, nodules in schistose gelsite.

Jack, R. Lockhart (1922) The iron ore resources of South Australia: S. Australia Geol. Surv. B. **9,** 71 pp. *S. Australia:* 1 granite.

Jack, R. Lockhart (1923) The building stones of South Australia: S. Australia Geol. Surv. B. **10,** 73 pp. *S. Australia:* 12; granite, marble, slate.

Jacobson, R. and T. R. Scott (1937) The geology of the Korkuperrimul Creek area, Bacchus Marsh: Roy. Soc. Victoria Proc. **50,** Pt. 1, 110–156. *Victoria:* 2; porphyritic basalt, olivine nephelinite.

James, Albert V. G. (1920) The physiography and geology of the Bulla–Sydenham area: Roy. Soc. Victoria Proc. **32,** Pt. 2, 323–349. *Victoria:* 1 granodiorite.

Johns, R. Keith and J. M. Kruger (1949) The Murray Bridge and Monarto granites and associated rocks of the metamorphic aureole: Roy. Soc. S. Australia Tr. **73,** Pt. 1, 122–136 *S. Australia:* 4; adamellite, granite.

Johnstone, Murray H. (1952) The geology of the Hamersley Siding area: Roy. Soc. W. Australia J. **36,** 45–75. *W. Australia:* 1 appinite.

Joplin, Germaine A. (1931) Petrology of the Hartley district. I. The plutonic and associated rocks: Linnean Soc. New South Wales Proc. **56,** No. 234, 16–59. *New South Wales:* 11; biotite granite, porphyritic biotite granite, granodiorite, tonalite, quartz diorite (monzonitic), quartz-mica diorite, diorite-gabbro, pyroxene gabbro, hornblendeite, aplite.

Joplin, Germaine A. (1933) The petrology of the Hartley district. II. The metamorphosed gabbros and associated hybrid and contaminated rocks: Linnean Soc. New South Wales Proc. **58,** No. 247–248, 125–158. *New South Wales:* 2 pyroxene gabbro.

Joplin, Germaine A. (1935) The petrology of the Hartley district. III. The contact metamorphism of the Upper Devonian (Lambian) Series: Linnean Soc. New South Wales Proc. **60,** No. 257–258, 16–50. *New South Wales:* 6; porphyrite (metamorphosed), andalusite-cordierite hornfels, cordierite-quartz-biotite hornfels, cordierite-plagioclase hornfels, biotite-plagioclase hornfels, wollastonite-orthoclase-diopside hornfels.

Joplin, Germaine A. (1936) The endogenous contact-zone of the magnesian limestones at Ben Bullen, N.S.W.: Roy. Soc. New South Wales J. and Proc. **69,** Pt. 2, 135–158. *New South Wales:* 3; quartz-mica diorite, diopside-zoisite-plagioclase rock, pyroxene-chlorite-spinel rock.

Joplin, Germaine A. (1937a) The petrology of the Hartley district. IV. The altered dolerite dykes: Linnean Soc. New South Wales Proc. **62,** No. 273–274, 263–268. *New South Wales:* 1 dolerite (altered).

Joplin, Germaine A. (1937b) The Ben Bullen plutonic complex, N.S.W.: Roy. Soc. New South Wales J. and Proc. **70,** Pt. 1, 69–94. *New South Wales:* 4; hornblende olivine norite, hornblende norite, pyroxene gabbro, quartz pyroxene diorite.

Joplin, Germaine A. (1939) Studies in metamorphism and assimilation in the Cooma district of New South Wales. Part I. The amphibolites and their metasomatism: Roy. Soc. New South Wales J. and Proc. **73,** Pt. 2, 86–106. *New South Wales:* 3 amphibolite.

Joplin, Germaine A. (1942) Petrological studies in the Ordovician of New South Wales. I. The Cooma complex: Linnean Soc. New South Wales Proc. **67,** No. 301–302, 156–196. *New South Wales:* 24; slate, chiastolite slate, quartz-chlorite-mica schist, chlorite-sericite phyllite, mica schist, andalusite schist, tuffaceous psammite, amphibole granulite, schist granulite, hornblende-pyroxene granulite, hornblende granulite, gneiss, pegmatite, albite-muscovite gneiss, chlorite amphibolite.

Joplin, Germaine A. (1943) Petrological studies in the Ordovician of New South Wales. II The northern extension of the Cooma complex: Linnean Soc. New South Wales Proc. **68,** No. 309–310, 159–183. *New South Wales:* 4; rhyolite, gneiss, quartz-mica diorite, quartz diorite.

Joplin, Germaine A. (1944) Petrology of the Hartley district. V. Evidence of hybridization in the Moyne Farm intrusion; a revision: Linnean Soc. New South Wales Proc. **69,** No. 313–314, 129–138. *New South Wales:* 2; granite porphyry, hybrid rock.

Joplin, Germaine A. (1945) Petrological studies in the Ordovician of New South Wales. III The composition and origin of the Upper Ordovician grapholite-bearing slates: Linnean Soc. New South Wales Proc. **70,** No. 319–320, 158–172. *New South Wales:* 8; slate, chiastolite slate, schist, gneiss (paragneiss).

Joplin, Germaine A. (1947) Petrological studies in the Ordovician of New South Wales. IV. The northern extension of the north-east Victorian metamorphic complex: Linnean Soc. New South Wales Proc. **72,** No. 331–332, 87–124. *New South Wales:* 16; slate, seritite schist, pyroxene granulite, basic rock (altered), garnet-bearing oligolcase granite, oligoclase-microcline granite, pegmatite, pegmatite (albitized), cordierite gneiss, gneiss, granite, sillimanite-cordierite-spinel xenolith.

Junner, Norman R. (1914) The petrology and mining geology of the country near Queenstown: Roy. Soc. Victoria Proc. **27,** Pt. 1, 119–147. *Victoria:* 2 quartz diorite.

Junner, Norman R. (1915) The petrology of the igneous rocks near Healesville and Narbethong: Roy. Soc. Victoria Proc. **27,** Pt. 2, 261–285. *Victoria:* 2; dacite, rhyolite.

Junner, Norman R. (1920) The geology and ore deposits of the Walhalla–Wood's Point auriferous belt: Australasian Inst. Min. Met. Proc. **39,** 127–258. *Victoria:* 8; basalt (porphyritic), perknite, diorite porphyrite (altered), hornblende mica lamprophyre (altered), dike (altered).

Jutson, John T. (1914) The mining geology of Ora Banda, Broad Arrow goldfield: W. Australia Geol. Surv. B. **54,** 134 pp. *W. Australia.:* 2; norite, serpentine.

Jutson, John T. (1921a) The mining geology of Kookynie, Niagara and Tampa, North Coolgardie goldfield: W. Australia Geol. Surv. B. **78,** 88 pp. *W. Australia:* 4; epidiorite, quartz porphyry, biotite granite.

Jutson, John T. (1921b) The mining geology of Comet Vale and Goongarrie, North Coolgardie goldfield: W. Australia Geol. Surv. B. **79,** 76 pp. *W. Australia:* 2 serpentine.

Keble, Robert A. (1950) The Mornington peninsula: Victoria Geol. Surv. Mem. **17,** 84 pp. *Victoria:* 1 granite.

Keble, Robert A. and John C. Watson (1952) Clay and shale deposits of Victoria (Part 1): Victoria Geol. Surv. Mem. **18,** 76 pp. *Victoria:* 1 granodiorite.

Kleeman, Alfred W. (1934a) An adamellite from "The Granites", Northern Territory: Roy. Soc. S. Australia Tr. **58,** 234–236. *Northern Territory:* 1 adamellite.

Kleeman, Alfred W. (1934b) The Murray Bridge granite: Roy. Soc. S. Australia Tr. **58,** 237–241. *S. Australia:* 2; granite, granite aplite.

Kleeman, Alfred W. (1936) The Artracoona meteorite: Roy. Soc. S. Australia Tr. **60,** 73–75. *S. Australia:* 1 meteorite.

Kleeman, Alfred W. (1937) The nature and origin of the so-called diorite inclusions in the granite of Granite Island: Roy. Soc. S. Australia Tr. **61,** 207–220. *S. Australia:* 4; adamellite porphyry, quartz-mica-hornblende diorite, hornfels inclusion.

Mahony, Daniel J. and T. G. Taylor (1913) Report on geological reconnaissance of the Federal Territory. 57 pp., Melbourne, Australia. *Capital Territory:* 2; granite, quartz porphyry. (As this report has limited distribution and is difficult to obtain, the analysis of the quartz prophyry is also indicated under E. O. Teale (1920) where it is reprinted).

Mahony, Daniel J. (1925a) Bullengarook slate quarry, near Gisborne: Victoria Geol. Surv. Rec. **4,** Pt. 4, 455–456. *Victoria:* 1 slate.

Mahony, Daniel J. (1925b) Petrology (Appendix). *In* The Aberfeldy district, Gippsland: Victoria Geol. Surv. Mem. **15,** 39–45. *Victoria:* 8; augite prophyry, feldspar porphyry, olivine andesite, orthoclase gabbro, limburgite, basalt, olivine pyroxene xenolith.

Mahony, Daniel J. (1931) Alkaline Tertiary rocks near Trentham and at Drouin, Victoria: Roy. Soc. Victoria Proc. **43,** Pt. 2, 123–129. *Victoria:* 5; trachyte, trachyphonolite, olivine nephelinite.

Mahony, Daniel J. (1936) Granite near Lake Boga: Victoria Geol. Surv. Rec. **5,** Pt. 2, 259–260. *Victoria:* 1 granite.

Maitland, A. Gibb (1925) Notes on the country in the vicinity and to the northward of Israelite Bay, Eucla division: W. Australia Geol. Surv. Ann. Prog. Rpt. 1942, 4–9. *W. Australia:* 10; soda granite, biotite gneiss, microcline biotite gneiss, garnet gneiss, quartz sericite schist norite.

Mawson, Douglas (1926) The Wooltana basic igneous belt: Roy. Soc. S. Australia Tr. **50,** 192–200. *S. Australia:* 3; melaphyre, olivine diabase.

Mawson, Douglas (1934) The Arltunga and Karoonda meteorites: Roy. Soc. S. Australia Tr. **58,** 1–6. *S. Australia:* 2 meteorites.

Mawson, Douglas (1942) The structural character of the Flinders Ranges: Roy. Soc. S. Australia Tr. **66,** 262–272. *S. Australia:* 2; melaphyre, meta-dolerite.

Mawson, Douglas and Leslie W. Parkin (1943) Some granitic rocks of south-eastern South Australia: Roy. Soc. S. Australia Tr. **67,** 233–243. *S. Australia:* 3; biotite granite, biotite granodiorite, hornblende-biotite granite.

Mawson, Douglas and Walter B. Dallwitz (1944a) Palaeozoic igneous rocks of lower south-eastern South Australia: Roy. Soc. S. Australia Tr. **68,** 191–209. *S. Australia:* 5; quartz keratophyre, potash-soda granite, potash-soda microgranite, potash-soda aporhyolite.

Mawson, Douglas (1944b) The nature and occurrence of uraniferous mineral deposits in South Australia: Roy. Soc. S. Australia Tr. **68,** 334–357. *S. Australia:* 2; soda granite, plagioclase amphibolite.

Mawson, Douglas and Walter B. Dallwitz (1945a) The soda-rich leucogranite cupolas of Umberatana: Roy. Soc. S. Australia Tr. **69,** 22–49. *S. Australia:* 3; muscovite-albite-microcline leucogranite, albite-microcline-tourmaline leucogranite, albite-microcline leucogranite.

Mawson, Douglas and E. Ralph Segnit (1945b) Porphyritic potash-soda microgranites of Mount Monster: Roy. Soc. S. Australia Tr. **69,** 217–222. *S. Australia:* 3 potash-soda microgranites.

Mawson, Douglas and E. Ralph Segnit (1945c) Granites of the Tintinara district: Roy. Soc. S. Australia Tr. **69,** 263–276, *S. Australia:* 3; potash-soda granite, potash-soda leucogranite, hornblende-biotite-adamellite.

Mawson, Douglas and E. Ralph Segnit (1946) Barium-rich aplitic gneisses of Broken Hill: Roy. Soc. S. Australia Tr. **70,** 277–293. *New South Wales:* 2; barium-rich gneiss, flaser gneiss.

Mawson, Douglas and E. Ralph Segnit (1949) Purple slates of the Adelaide System: Roy. Soc. S. Australia Tr. **72,** Pt. 2, 276–280. *S. Australia:* 1 slate.

Mawson, Douglas (1950) Basaltic lavas of the Balleny Islands, A.N.A.R.E. Report: Roy. Soc. S. Australia Tr. **73,** Pt. 2, 223–231. *Antarctica:* 2 olivine trachybasalt.

McCance, Donald M. (1932) Weathering of the "Older Basalt" of Royal Park: Roy. Soc. Victoria Proc. **44,** Pt. 2, 243–256. *Victoria:* 3 basalt.

McInerny, Kathleen (1929) The building stones of Victoria: Part II. The igneous rocks: Roy. Soc. Victoria Proc. **41,** Pt. 2, 121–159. *Victoria:* 1 basalt.

McMath, John C. (1950) Note on monazite in Cape Riche pegmatites: W. Australia Geol. Surv. Rpt. 1948, 33. *W. Australia.:* 1 injection gneiss.

McWhae, J. Ross H. (1948) The geology and physiography of the Lawnswood area: Roy. Soc. W. Australia J. **32,** 49–74. *W. Australia:* 1 quartz-plagioclase epidote chlorite rock.

Miles, Keith R. (1943) Some kyanite-bearing rocks from the eastern goldfields, Western Australia: Roy. Soc. W. Australia J. **27,** 9–25. *W. Australia:* 1 quartz-muscovite schist.

Mingaye, John C. H. (1916a) Notes from the Chemical Laboratory: New South Wales Geol. Surv. Rec. **9,** Pt. 3, 127–135. *New Hebrides:* 1 basalt.

Mingaye, John C. H. (1916b) Notes on the composition of the Delegate meteorite: New South Wales Geol. Surv. Rec. **9,** Pt. 3, 158–161. *New South Wales:* 1 meteorite.

Mingaye, John C. H. (1916c) Notes on the Molong meteorite: New South Wales Geol. Surv. Rec. **9,** Pt. 3, 161–165. *New South Wales:* 1 meteorite.

Mingaye, John C. H. (1916d) Notes on Gilgoin meteorite, No. 7, Brewarrina, New South Wales: New South Wales Geol. Surv. Rec. **9,** Pt. 3, 166–170. *New South Wales:* 1 meteorite.

Mingaye, John C. H. (1916e) Analyses of obsidianites from the Uralla district and Charelott Waters: New South Wales Geol. Surv. Rec. **9,** Pt. 3, 170–171. *New South Wales:* 2 obsidianite.

Mingaye, John C. H. (1920) Description of an iron meteorite found at Yenberrie, Northern Territory: Chem. Eng. Min. Rev. **13,** 48. *Northern Territory:* 3 meteorites.

Mingaye, John C. H. (1921) The Warialda meteorite: New South Wales Geol. Surv. Rec. **10,** Pt. 1, 75–78. *New South Wales:* 1 meteorite.

Morris, Morris (1914) On the geology and petrology of the district between Lilydale and Mount Dandenong: Roy. Soc. Victoria Proc. **26,** Pt. 2, 331–366. *Victoria:* 4; toscanite, dacite.

New South Wales Geological Survey (1916) Annual report of the Government Geologist: New South Wales Dept. Mines, Ann. Rpt. 1915, 172–199. *New South Wales:* 3; dolerite, marble.

New South Wales Geological Survey (1917) Annual report of the Government Geologist: New South Wales Dept. Mines, Ann. Rpt. 1916, 189–229. *New South Wales:* 2; norite, kersantite.

New South Wales Geological Survey (1918) Annual report of the Government Geologist: New South Wales Dept. Mines, Ann. Rpt. 1917, 152–184. *New South Wales:* 3 tuff.

New South Wales Geological Survey (1919) Annual report of the Government Geologist: New South Wales Dept. Mines, Ann. Rpt. 1918, 152–171. *New South Wales:* 1 quartz porphyry.

New South Wales Geological Survey (1920) Annual report of the Government Geologist: New South Wales Dept. Mines, Ann. Rpt. 1919, 160–188. *New South Wales:* 2; felsite (altered), sandstone (altered).

New South Wales Geological Survey (1921) Annual report of the Government Geologist: New South Wales Dept. Mines, Ann. Rpt. 1920, 97–126. *New South Wales:* 5 slate.

New South Wales Geological Survey (1923) Annual report of the Government Geologist: New South Wales Dept. Mines, Ann. Rpt. 1922, 87–104. *New South Wales:* 1 garnet sandstone.

New South Wales Geological Survey (1924) Annual report of the Government Geologist: New South Wales Dept. Mines, Ann. Rpt. 1923, 77–102. *New South Wales:* 12; andesite, cortlandite, hornblende andesite, pyroxene andesite, dacite, rhyolite, syenite, pegmatite, nephelite basalt.

New South Wales Geological Survey (1925) Annual report of the Government Geologist: New South Wales Dept. Mines, Ann. Rpt. 1924, 82–107. *New South Wales:* 4; meteorite, dike rock, trachytic rock, slate.

New South Wales Geological Survey (1926) Annual report of the Government Geologist: New South Wales Dept. Mines, Ann. Rpt. 1925, 90–144. *New South Wales:* 2 lamporphyric rock.

New South Wales Geological Survey (1927) Annual report of the Government Geologist: New South Wales Dept. Mines, Ann. Rpt. 1926, 93–105. *New South Wales:* 3; colerite, nephelite basalt, quartz porphyry.

New South Wales Geological Survey (1929) Annual report of the Government Geologist: New South Wales Dept. Mines, Ann. Rpt. 1928, 93–140. *New South Wales:* 1 dolerite.

New South Wales Geological Survey (1931) Annual report of the Government Geologist: New South Wales Dept. Mines, Ann. Rpt. 1930, 75–88. *New South Wales:* 2; dolerite, syenite.

New South Wales Geological Survey (1933) Annual report of the Government Geologist: New South Wales Dept. Mines, Ann. Rpt. 1932, 78–97. *New South Wales:* 1 granite.

New South Wales Geological Survey (1935) Annual report of the Government Geologist: New South Wales Dept. Mines, Ann. Rpt. 1934, 76–101. *New South Wales:* 2; dolerite, syenite

Nye, Percival B. (1923) The silver-lead deposits of the Waratah district: Tasmania Geol. Surv. B. **33,** 1–88. *Tasmania:* 2; syenite, syenite porphyry.

Nye, Percival B., Kevin J. Finucane and Frank Blake (1934) The Smithton district: Tasmania Geol. Surv. B. **41,** 116 pp. *Tasmania:* 9; dolerite, gabbro, mugearite, augite porphyrite, dolerite porphyrite, olivine basalt.

Orr, D. (1928) An olivine anorthoclase basalt from Daylesford: Roy. Soc. Victoria Proc. **40,** Pt. 1, 34–44. *Victoria:* 1 anorthoclase olivine basalt.

Osborne, George D. (1920) The volcanic neck at the Basin, Nepean River: Roy. Soc. New South Wales J. and Proc. **54,** 113–145. *New South Wales:* 2; dunite, troctolite.

Osborne, George D. (1925) The geology and petrography of the Clarencetown–Paterson district. Part 4, Petrography: Linnean Soc. New South Wales Proc. **50,** No. 201, 112–138. *New South Wales:* 4; dellenite, andesite, quartz keratophyre.

Osborne, George D. (1949) Contributions to the study of the Marulan batholith. Part 1. The contaminated granodiorites of South Marulan and Marulan Creek: Roy. Soc. New South Wales J. and Proc. **82,** Pt. 2, 116–128. *New South Wales:* 4; granodiorite, andalusite-cordierite spinel-plagioclase xenolith, biotite-hornblende xenolith.

Osborne, George D. and John F. Lovering (1953) Contributions to a study of the Marulan batholith. II. The granodiorite-quartz porphyrite hybrids: Roy. Soc. New South Wales J. and Proc. **86,** Pt. 4, 108–118. *New South Wales:* 2 hybrid rocks (from quartz porphyrites).

Prider, Rex T. (1943) The contact between the granitic rocks and the Cardup Series at Armadale: Roy. Soc. W. Australia J. **27,** 27–55. *W. Australia:* 8; quartz dolerite, sericite schist biotite epidiorite, chlorite-albite epidiorite, slate, gneiss, hornblende-epidote-biotite hornfels xenolith.

Prider, Rex T. (1944) The geology and petrology of part of the Toodyay district, Western Australia: Roy. Soc. W. Australia J. **28,** 83–137. *W. Australia:* 7; plagioclase amphibolite, quartz-plagioclase amphibolite, hornblende granite gneiss, biotite-microcline granite gneiss, biotite-oligoclase granite gneiss, serpentine.

Prider, Rex T. (1945) Granitic rocks from Canning Dam: Roy. Soc. W. Australia J. **29,** Pt. 1, 137–149. *W. Australia:* 2; granite, epidote-biotite xenolith.

Rattigan, John H. and Clemens F. Wegener (1951) Granites of the Palmer area and associated granitized sediments: Roy. Soc. S. Australia Tr. **74,** Pt. 2, 149–164. *S. Australia:* 2; granite, gneiss.

Rayner, Jack Maxwell (1939) Geophysical report on the Henbury meteorite craters, Central Australia: Aerial, Geol. and Geophys. Surv. N. Australia Rpt. **42,** 7 pp. *Northern Territory:* 1 meteorite.

Reid, Alexander M. (1923) The Mount Bischoff tin field: Tasmania Geol. Surv. B. **34,** 167 pp. *Tasmania:* 24; quartz porphyry, quartz porphyry (altered), quartz porphyry (topazised), pyroxenite (altered), dolomitized rock, mineralized rock.

Reid, Alexander M. and Q. J. Henderson (1928) Blue Tier tin field: Tasmania Geol. Surv. B. **38,** 128 pp. *Tasmania:* 6; granite (porphyritic), granite (altered), granite (tin-bearing), granite (fluorite-bearing).

Reid, John H. (1917) The Charters Towers goldfield: Queensland Geol. Surv. Pub. **256,** 236 pp. *Queensland:* 9; granodiorite, diorite, quartz diorite, quartz porphyry, diorite porphyrite, hornblended prophyrite, granite (aplitic).

Richards, Henry C. (1918a) The building stones of Queensland: Roy. Soc. Queensland Proc. **30,** 97–157. *Queensland:* 1 granite.

Richards, Henry C. (1918c) The volcanic rocks of Springsure, central Queensland: Roy. Soc. Queensland Proc. **30,** 179–198. *Queensland:* 3; basalt, fayalite basalt, phonolite.

Richards, Henry C. (1923a) Anorthoclase basalt from Mapleton, Blackall Range, south-eastern Queensland: Roy. Soc. Queensland Proc. **34,** 161–167. *Queensland:* 2; basalt, anorthoclase basalt.

Richards, Henry C. (1923b) An unusual rhyolite from the Blackall Range, south-eastern Queensland: Roy. Soc. Queensland Proc. **34,** 195–208. *Queensland:* 1 rhyolite.

Richards, Henry C. and Walter H. Bryan (1924) Permo-Carboniferous volcanic activity in southern Queensland: Roy. Soc. Queensland Proc. **35,** 109–126. *Queensland:* 5; andesite, basalt, rhyolite, rhyolite tuff.

Richards, Henry C. (1925a) A geological reconnaissance in north Queensland: Great Barrier Reef Committee Rpt. **1,** 1–28. *Queensland:* 1 quartz feldspar prophyry.

Richards, Henry C. and Walter H. Bryan (1925b) The geology of the Silverwood-Lucky Valley area: Roy. Soc. Queensland Proc. **36,** 44–108. *Queensland:* 3; andesite, spilite, rhyolitic dike.

Richards, Henry C. (1930) The Glenormiston meteorite: Queensland Mus. Mem. **10,** Pt. 1, 65–72. *Queensland:* 1 meteorite.

Ridgway, John E. (1952) Clay deposit for brickmaking, Slape Gully: S. Australia Dept. Mines, Min. Rev. **92,** 29–35. *South Australia:* 4 slate.

Robinson, Edwin G. (1949) The petrological nature of some rocks from the Mann, Tompkinson and Ayres Ranges of Central Australia: Roy. Soc. S. Australia Tr. **73,** Pt. 1, 29–39. *South Australia:* 2; hypersthenite, diopside peridotite.

Saint-Smith, E. Cecil (1917) On the occurrence of white marble at South Ulam, Rockhampton district: Queensland Govt. Min. J. **18,** No. 211, 596–599. *Queensland:* 1 marble.

Scott, Beryl (1951) The petrology of the volcanic rocks of south-east King Island, Tasmania: Roy. Soc. Tasmania Papers and Proc. 1950 113–136. *Tasmania:* 7; glass, tuff, spilite, picrite basalt.

Scott, Beryl (1952) The occurrence of pillow lavas near Penguin, Tasmania: Roy. Soc. Tasmania Papers and Proc. **86,** 123–125. *Tasmania:* 1 spilite.

Segnit, E. Ralph (1949) A soda-rich composite intrusive stock located in the Boolcoomatta Hills, South Australia: Roy. Soc. S. Australia Tr. **73,** Pt. 1, 109–112. *S. Australia:* 2; essexite, albite syenite.

Sherrard, Kathleen (1952) The geology of the Nanima–Bedulluck district, near Yass, New South Wales: Roy. Soc. New South Wales J. and Proc. **85,** Pt. 2, 63–81. *New South Wales:* 4; rhyolite, dacite, porphyry, quartz prophyry.

Simpson, Edward S. (1914a) The deposition of gold in the Gimlet ore-vein and the accompanying chemical changes in the adjacent rock, *in* The mining geology of Ora Banda, Broad Arrow goldfield: W. Australia Geol. Surv. B. **54,** 95–109. *Western Australia:* 4; hornblende porphyrite, prophyrite (altered), hornblende porphyrite (altered).

Simpson, Edward S. and Harry Bowley (1914b) Some Western Australian meteorites. I. Premier Downs. II. A new meteorite from Western Australia: W. Australia Geol. Surv. B. **59,** 205–209. *W. Australia:* 1 meteorite.

Simpson, Edward S. (1914c) Some Western Australian meteorites. II. Preliminary note on the Mount Edith meteorite: W. Australia Geol. Surv. B. **59,** 210–212. *W. Australia:* 1 meteorite.

Simpson, Edward S. (1916) Analyses of Western Australian rocks, meteorites and natural waters: W. Australia Geol. Surv. B. **67,** 196 pp. *W. Australia:* 77; various igneous and metamorphic types.

Simpson, Edward S. (1921) Notes on staurolite from the Mogumber district: Roy. Soc. W. Australia J. and Proc. **7,** 71–74. *W. Australia:* 1 staurolite schist.

Simpson, Edward S. (1930) Contributions to the mineralogy of Western Australia, series V: Roy. Soc. W. Australia J. and Proc. **16,** 25–40. *W. Australia:* 2; chlorite rock; chlorite schist.

Simpson, Edward S. (1931) Contributions to the mineralogy of Western Australia, series VI: Roy. Soc. W. Australia J. and Proc. **17,** 137–149. *W. Australia:* 1 cummingstonite schist.

Simpson, Edward S. (1933) The occurrence of andalusite, kyanite, sillimanite and staurolite in the Chittering Valley: Roy. Soc. W. Australia J. and Proc. **18,** 75–82. *W. Australia* 1 staurolite schist.

Simpson, Edward S. (1937) Contributions to the mineralogy of Western Australia: Roy. Soc. W. Australia J. and Proc. **23,** 17–35. *W. Australia:* 4; anthophyllite rock, chloritoid mica schist, garnet hornstone.

Simpson, Edward S. (1938) Contributions to the mineralogy of Western Australia, series XI: Roy. Soc. W. Australia J. and Proc. **24,** 107–122. *W. Australia:* 2; cordierite-anthophyllite rock, fayalite gabbro.

Skeats, Ernest W. and Albert V. G. James (1937) Basaltic barriers and other surface features of the newer basalts of western Victoria: Roy. Soc. Victoria Proc. **49,** Pt. 2, 245–278. *Victoria:* 2 basalt.

Spry, Alan H. (1951) The Archean complex at Houghton, South Australia: Roy. Soc. S. Australia Tr. **74,** Pt. 1, 115–134. *S. Australia:* 1 adamellite.

Stevens, Neville C. (1952) The petrology of the Cowra intrusion and associated xenoliths: Linnean Soc. New South Wales Proc. **77,** No. 361–362, 132–141. *New South Wales:* 8; granodiorite, granodiorite porphyry (garnetiferous), hypersthene:plagioclase-biotite-quartz xenolith, cordierite-sillimanite-spinel xenolith, slate.

Stillwell, Frank L. (1919) The factors influencing gold deposition in the Bendigo goldfield. Part III: Commonwealth of Australia, Advisory Council of Science and Industry B. **16,** 36 pp. *Victoria:* 1 slate.

Stillwell, Frank L. (1922) The rocks in the immediate neighbourhood of the Broken Hill lode and their bearing on its origin, Appendix II. In the geology of the Broken Hill district: New South Wales Geol. Surv. Mem. **8,** 354–396. *New South Wales:* 37; amphibolite, garnet amphibolite, garnet sandstone, gneiss, garnet-plagioclase gneiss, garnet-sillimanite-cordierite schist, sillimanite-cordierite gneiss, quartzite, aplite gneiss, platy gneiss, augen-gneiss.

Stillwell, Frank L. (1929) Geology and ore deposits of the Boulder Belt, Kalgoorlie: W. Australia Geol. Surv. B. **94,** 110 pp. *W. Australia:* 6; quartz dolerite greenstone, labite porphyry, basic prophyrite, porphyrite (altered), "slate".

Summers, Herbert S. (1914a) On the composition and origin of australites: Australasian Assoc. Adv. of Science Rpt. 14th mtg., Melbourne 1913, 189–199. *New South Wales:* 1 australite; *Victoria:* 1 australite.

Summers, Herbert S. (1914b) On the origin and relationship of some Victorian igneous rocks Roy. Soc. Victoria Proc. **26,** Pt. 2, 256–297. *Victoria:* 8; adamellite, granite, granodiorite, hypersthene quartz porphyrite, epidiorite.

Sussmilch, Carl A. (1922) The geology of the Gloucester district of New South Wales: Roy. Soc. New South Wales J. and Proc. **55,** 234–262. *New South Wales:* 4; rhyolite, quartz keratophyre, keratophyre.

Sussmilch, Carl A. and William A. Greig (1929) The geology of Port Stephens, Part 2, Petrography: Roy. Soc. New South Wales J. and Proc. **62,** 181–191. *New South Wales:* 6; andesite, toscanite rhyolite.

Talbot, Henry W. B. (1920) A geological reconnaissance in the southern portion of the Yalgoo goldfield: W. Australia Geol. Surv. Ann. Prog. Rpt. 1919, 7–12. *W. Australia:* 1 quartz-kyanite rock.

Tattam, Charles M. (1929) The metamorphic rocks of north-east Victoria: Victoria Geol. Surv. B. **52,** 61 pp. *Victoria:* 14; slate, andalusite hornfels, cordierite hornfels, gneiss, pinite-sillimanite-biotite gneiss, pinite-biotite gneiss, granite, quartz-mica-diorite gneiss, feldspathic pinite gneiss, schist xenolith, micaceous xenolith.

Teale, Edmund O. (1916) See Thiele, E. O. (1916).

Teale, Edmund O. (1919) The diabases and associated rocks of the Howqua River near Mansfield, with reference to the Heathcotian problem in Victoria: Roy. Soc. Victoria Proc. **32,** Pt. 1, 33–66. *Victoria:* 3 diabase.

Teale, Edmund O. (1920) A contribution to the Palaeozoic geology of Victoria, with special reference to the districts of Mount Wellington and Nowa Nowa respectively: Roy. Soc. Victoria Proc. **32,** Pt. 2, 67–146. *Victoria:* 4; quartz porphyrite, melaphyre, tuff; *Capital Territory:* 1; quartz porphyry. (Reprint; see note under Mahony and Taylor, 1913.)

Terrill, Stanley E. (1950) Notes on laterite in the Darling Range near Perth, Western Australia: Roy. Soc. W. Australia J. **34,** 105–110. *Western Australia:* 1 dolerite.

Thiele, Edmund O. (same as Teale, Edmund O., see above) (1916) Petrographical notes on the igneous rocks of Mount Remarkable. *In* The geology of Mount Remarkable: Roy. Soc. S. Australia Tr. **40,** 580–583. *S. Australia:* 1 quartz keratophyre; *Victoria:* 1 quartz keratophyre.

Thomas, David E. (1942) The conglomerates in the Gould–Platina districts, Gippsland, Victoria: Min. Geol. J. **2,** No. 6, 357–360. *Victoria:* 1 igneous rock.

Thomas, David E. (1947) The geology of the Eildon dam projects: Victoria Geol. Surv. Mem. **16,** 47 pp. *Victoria:* 6; basalt, rhyolite, biotite rhyodacite, toscanite, cordierite nevadite.

Thomson, Brendan P. (1943) The geology and physiography of the Wongong–Cardup area: Roy. Soc. W. Australia J. **27,** 265–283. *W. Australia:* 1 biotite hornfels xenolith.

Vallance, Thomas G. (1953a) Studies in the metamorphic and plutonic geology of the Wantabadgery–Adelong–Tumbarumba district, N.S.W. Part I. Introduction and metamorphism of the sedimentary rocks: Linnean Soc. New South Wales Proc. **78,** No. 367–368, 90–121. *New South Wales:* 15; granulite, quartz granulite, cordierite granulite, phyllite, psammopelite quartz psammite, schist, serpentine, ultrabasic inclusion.

Vallance, Thomas G. (1953b) Studies in the metamorphic and plutonic geology of the Wantabadgery–Adelong–Tumbarumba district N.S.W. Part II. Intermediate-basic rocks: Linnean Soc. New South Wales Proc. **78,** No. 368–370, 181–196. *New South Wales:* 3; amphibolite, "amphibolite" xenolith, albite-epidote-chlorite-calcite rock.

Vallance, Thomas G. (1953c) Studies in the metamorphic and plutonic geology of the Wantabadgery–Adelong–Tumbarumba district, N.S.W. Part III. The granitic rocks: Linnean Soc. New South Wales Proc. **78,** No. 369–370, 197–220. *New South Wales:* 8; biotite granite, biotite adamellite, granodiorite, aplite (garnetiferous).

Walcott, R. Henry (1915) Description of the Victorian meteorites, with notes on obsidianites: Natl. Mus. Melbourne Mem. **6,** 65 pp. *Victoria:* 3 meteorites.

Watson, John C. (1925) Cement tests with materials from Nowa Nowa: Victoria Geol. Surv. Rec. **4,** Pt. 4, 449–451. *Victoria:* 1 slate.

White, Harold P. (1920) Notes and analyses of the Hermitage Plains aerolite: New South Wales Geol. Surv. Rec. 9, Pt. 2, 108–109. *New South Wales:* 1 meteorite.

Wilson, Allan F. (1949) The charnockitic and associated rocks of north-western South Australia II. Dolerites from the Musgrave and Everard Ranges: Roy. Soc. S. Australia Tr. **72,** Pt. 2, 178–200. *S. Australia:* 1 olivine bronzite dolerite.

Winton, L. J. (1920) Report on the Australian slate quarry, Willunga: S. Australia Dept. Mines Min. Rev. **31,** 57–06. *S. Australia:* 1 slate.

Geographic Index

The index is arranged alphabetically by the states within Australia, further subdivided into local districts, and other areas from which rocks have been analysed and published in the Australian literature. The author names given for each of these areas relate to the bibliography where the full reference is given. The number that is given beside the name of each area or state is the total number of analyses for that area; the number of analyses in each reference is given in the bibliography.

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uralitized	Simpson 1916
Basanite, nepheline	Aurousseau 1926
Basic rock, altered	Joplin 1947
Basic xenolith	Brown 1928
Biotite-hornblende xenolith	Osborne 1949
Biotite-hornfels xenolith	Thomson 1943
Chlorite rock	Simpson 1930
Cordierite-anthophyllite rock	Simpson 1938
Cordierite-sillimanite-spinel xenolith	Stevens 1952
Cortlandtite	New South Wales G. S. 1924
Covite	Brown 1930
Crinanite	Edwards 1941b; 1953c
nepheline-rich	Edwards 1941b
olivine-rich	Edwards 1941b
Dacite	Junner 1915; Morris 1914; New South Wales G. S. 1924; Sherrard 1952
hypersthene	Edwards 1932a; 1937b
quartz	Edwards 1932a
α-quartz-biotite	Edwards 1932b
β-quartz-hypersthene-biotite	Edwards 1932a
Dellenite	Osborne 1925
Diabase	Teale 1919
olivine	Mawson 1926
Dike	Dunn 1914a
altered	Junner 1920; New South Wales G. S. 1925
basic	Alderman 1929, 1931
carbonated	Finucane 1935
rhyolitic	Richards and Bryan 1925b
Diopside-zoisite-plagioclase rock	Joplin 1936
Diorite	England 1935; Reid J. H. 1917; Simpson 1916
quartz	Brown 1928; England 1935; Joplin 1931, 1943;

Diorite (*continued*)	
quartz (*continued*)	Junner 1914; Reid J. H. 1917
quartz-augite	Edwards and Easton 1937a
quartz-mica	Browne 1920b; Bryan 1923; Joplin 1931, 1936
quartz-mica-hornblende	Kleeman 1937
quartz-mica, hornblende-free	Joplin 1943
quartz-pyroxene	Joplin 1937b
Diorite gabbro	Brown 1928; Joplin 1931
Diorite porphyrite	Reid J. H. 1917
altered	Junner 1920
propylitized	Junner 1920
Dolerite	Benson 1915a; 1918; Edwards 1947; England 1935; Grace 1948; Howard 1951; New South Wales G. S. 1916, 1929, 1931, 1935; Nye, Finucane and Blake 1934; Simpson 1916; Terrill 1950
altered	Basnett 1939; Joplin 1937a
analcite-olivine	Edwards 1953c
analcite-olivine-titanaugite	Edwards 1953c
hybridized	Basnett 1939
kaolinized	New South Wales G. S. 1927
labradorite	Benson 1915b
meta-	Mawson 1942
metamorphosed	Edwards 1947
olivine-analcite	Edwards 1934
olivine-bronzite	Wilson 1949
porphyritic	Benson 1918; Nye, Finucane and Blake 1934
quartz	Benson 1915a
quartz, two-pyroxene	Edwards 1943
quartz, uralitized	Prider 1943
titanaugite	Edwards 1953c
uralitic	Browne 1920b; 1922a; Edwards 1947; Simpson 1916
zoisitized	Farquharson 1914a
Dolerite amphibolite	Alderman 1931
Dolerite gabbro	Bowley 1945
Dolerite porphyrite	Nye, Finucane and Blake 1934
Dolomitized rock	Reid A. M. 1923
Dunite	Osborne 1920
Eclogite	Simpson 1916
Epidiorite	Chemical Staff 1922; Clarke and Williams 1927; Farquharson 1914a; 1917; Jutson 1921a; Simpson 1916; Summers 1914b
biotite	Prider 1943
chlorite-albite	Prider 1943
quartz	Bowley 1926
Epidosite	Browne 1922a; Simpson 1916
zoisite	Chemical Staff 1922
Epidote-biotite-xenolith	Prider 1945
Essexite	Segnit 1949
Felsite	New South Wales G. S. 1920
nodules	Jack 1917
schistose	Jack 1917
Fuchsite-quartz rock	Feldtmann 1935
Fuchsite-quartz-carbonate rock	Feldtmann 1916
Gabbro	Nye, Finucane and Blake 1934
fayalite	Simpson 1938
garnetized	Bowley 1945

Gabbro (*continued*)	
hornblende	Browne 1922a; Brown 1928
hornblende-hypersthene	Browne 1922a
hypersthene	Edwards and Crawford 1940
orthoclase	Mahony 1925b
pyroxene	Joplin 1931; 1933; 1937b
Garnet sandstone	Chemical Staff 1922; New South Wales G. S. 1923; Stillwell 1922
Garnet-quartz-magnetite rock	Browne 1922a
Glass	Scott 1951
Darwin	David, Summers and Ampt 1927
silica	Fenner 1940
Gneiss	Alderman 1938; Browne 1922a; Joplin 1942; 1943; 1945; 1947; Rattigan and Wegener 1951; Simpson 1916; Stillwell 1922; Tattam 1929
albite-muscovite	Joplin 1942
aplite	Stillwell 1922
augen-	Alderman 1938; Browne 1922a; Chemical Staff 1922; Jack 1914; Stillwell 1922
barium-rich	Mawson and Segnit 1946
biotite	Maitland 1925
cordierite	Joplin 1947
flaser	Mawson and Segnit 1946
garnet	Maitland 1925
garnet-plagioclase	Stillwell 1922
hornblende-quarta-feldspar-biotite	Farquharson 1917
hybrid	Prider 1943
injection	McMath 1950
microcline biotite	Maitland 1925
pegmatitic	Browne 1922a
pinite, felspathic	Tattam 1929
pinite-biotite	Tattam 1929
pinite-sillimanite-biotite	Tattam 1929
platy	Browne 1922a; Stillwell 1922
quartz-mica-diorite	Tattam 1929
sillimanite	Browne 1922a
sillimanite-cordierite	Stillwell 1922
Granite	Andrews 1916; Aurousseau 1926; Bowley 1948; Davis 1943; Edwards and Easton 1937a; Goode 1927; Hossfeld 1925; Jack 1914; 1922; 1923; Johns and Kruger 1949; Joplin 1947; Keble 1950; Kleeman 1934b; Mahony and Taylor 1913; Mahony 1936; New South Wales G. S. 1933; Prider 1945; Rattigan and Wegener 1951; Richards 1918a; Simpson 1916; Summers 1914b; Tattam 1929
altered	Reid A. M. and Henderson 1928
aplitic	Reid J. H. 1917
biotite	Andrews 116; Brown 1928; Edwards and Easton 1937a; Joplin 1931; Jutson 1921a; Mawson and Parkin 1943; Vallance 1953c
biotite, porphyritic	Joplin 1931
fluorite	Reid A. M. and Henderson 1928
hornblende-biotite	Mawson and Parkin 1943
leuco-, albite-microcline	Mawson and Dallwitz 1945a

Granite (*continued*)	
leuco-, albite-microcline-tourmaline	Mawson and Dallwitz 1945a
muscovite-albite-microcline	Mawson and Dallwitz 1945a
potash-soda	Mawson and Segnit 1945c
micro-, potash-soda	Mawson and Dallwitz 1944a
potash-soda, porphyritic	Mawson and Segnit 1945b
muscovite	Andrews 1916
oligoclase, garnet-bearing	Joplin 1947
oligoclase-microcline	Joplin 1947
porphyritic	Browne 1920b; Reid A. M. and Henderson 1928
potash-soda	Mawson and Dallwitz 1944a; Mawson and Segnit 1945c
soda	Maitland 1925; Mawson 1944b; Simpson 1916
tin-bearing	Reid A. M. and Henderson 1928
Granite aplite	Kleeman 1934b
Granite gneiss	
biotite-microcline	Prider 1944
biotite-oligoclase	Prider 1944
hornblende	Prider 1944
Granite porphyry	Broadhurst and Campbell 1933; Brown 1928; Joplin 1944
Granodiorite	Baker 1942; Broadhurst and Campbell 1933; Brown 1928; Edwards 1932b; James 1920; Joplin 1931; Keble and Watson 1952; Osborne 1949; Reid J. H. 1917; Simpson 1916; Stevens 1952; Summers 1914b; Vallance 1953c
biotite	Mawson and Parkin 1943
kaolinized	Gaskin 1944
porphyritic	Edwards and Baker 1944b
Granodiorite porphyry	Stevens 1952
Granulite	Chemical Staff 1922; Joplin 1942; Vallance 1953a
amphibole	Joplin 1942
cordierite	Vallance 1953a
hornblende	Joplin 1942
hornblende-pyroxene	Joplin 1942
pyroxene	Joplin 1947
quartz	Vallance 1953a
Graphitic rock	Feldtmann 1935
Greenstone	Feldtmann 1916
quartz-dolerite	Feldtmann 1916; Stillwell 1929
quartz-dolerite-tourmaline	Feldtmann 1916
Greywacke, tuffaceous	Edwards and Glaessner 1953b
Hornblende-epidote-biotite-hornfels xenolith	Prider 1943
Hornblendite	Joplin 1931
Hornfels	
andalusite	Tattam 1929
andalusite-cordierite	Joplin 1935
biotite	Thomson 1943
biotite-plagioclase	Joplin 1935
cordierite	Tattam 1929
cordierite-plagioclase	Joplin 1935
cordierite-quartz-biotite	Joplin 1935

Hornfels (*continued*)	
hornblende-epidote-biotite	Prider 1943
wollastonite-orthoclase-diopside	Joplin 1935
xenolith	Kleeman 1937
Hornstone, garnet	Simpson 1937
Hybrid rock	Osborne and Lovering 1953
leucocratic	Edwards 1947
melanocratic	Edwards 1947
porphyritic	Joplin 1944
soda	Alderman 1938
spotted	Basnett 1939
Hypersthene-plagioclase-biotite-quartz xenolith	Stevens 1952
Hypersthenite	Robinson 1949
Igneous rock	Thomas 1942
Intrusive, dark	Browne and White 1929
Kedabekite	Brown 1930
Keratophyre	Basnett 1939; Benson 1915a; Simpson 1916; Sussmilch 1922
magnetite	Benson 1915a
quartz	Benson 1915b; Browne 1920a; Mawson and Dallwitz 1944a; Osborne 1925; Sussmilch 1922; Thiele 1916
Kersantite	New South Wales G. S. 1917
Lamprophyre	Bowley 1926
hornblende-mica, altered	Junner 1920
hornblende-mica, propylitized	Junner 1920
Lamprophyric rock	New South Wales G. S. 1926
Latite, acid	Chalmers 1941
Leucitite	Blatchford 1927
Limburgite	Edwards and Crawford 1940; Edwards 1950; Mahony 1925b
Marble	Jack 1923; New South Wales G. S. 1916; Saint-Smith 1917
Melaphyre	Mawson 1926; 1942; Teale 1920
Melteigite, melanite	Brown 1930
Mesitite, talc	Feldtmann 1916
Meteorite	Aldermann 1932; 1936; 1940; Anderson and Mingaye 1913; Edwards and Baker 1942; 1944a; 1946; 1953a; Hodge-Smith and White 1926; Hodge-Smith 1929; 1931; 1932; 1937; Hodge-Smith and Chalmers 1942; Kleeman 1936; Mawson 1934; Mingaye 1916b; 1916c; 1916d; 1920; 1921; New South Wales G. S. 1925; Rayner 1939; Richards 1930; Simpson and Bowley 1914b; Simpson 1914c; Walcott 1915; White 1920
Micaceous xenolith	Tattam 1929
Mineralized rock	Reid A. J. 1923
Monchiquite	Edwards 1934; Harvey and Joplin 1941
biotite-free	Harvey and Joplin 1941
biotite-rich	Harvey and Joplin 1941
Monchiquite basalt	Edwards 1934
Monzonite	Brown 1930
olivine	Brown 1930
quartz	Browne and Greig 1922b
Monzonite porphyry	Browne and Greig 1922b

Mugearite	Nye, Finucane and Blake 1934
Nephelinite, olivine	Edwards 1934; 1950; Jacobson and Scott 1937; Mahony 1931
Nevadite, cordierite	Hills 1929; Thomas 1947
Norite	Jutson 1914; Maitland 1925; New South Wales G. S. 1917; Simpson 1916
biotite	Alderman 1927
hornblende	Joplin 1937b
hornblende-olivine	Joplin 1937b
quartz	Chemical Staff 1922
Olivine-pyroxene xenolith	Mahony 1925b
Orthoclasite, garnet	Edwards 1947
Pegmatite	Joplin 1942; 1947; New South Wales G. S. 1924
albitized	Joplin 1947
soda	Simpson 1916
syenite	Edwards 1947
Perioditite	
carbonated	Simpson 1916
diopside	Robinson 1949
Perknite	Junner 1920
orthoclase	Mahony 1925b
Phlogopite-olivine rock	Hayton 1950
Phonolite	Richards 1918b
Phyllite	Andrews 1915; Simpson 1916; Vallance 1953b
chlorite-sericite	Joplin 1942
sericite	Farquharson 1916
Picrite	Edwards 1953c
Picrite basalt	Scott 1951
Picritic rock	Edwards 1953c
Porphyrite	Simpson 1916
albite, carbonated	Feldtmann 1916
altered	Simpson 1914a; Stillwell 1929
augite	Colditz 1948
augite, altered	Nye, Finucane and Blake 1934
basic	Stillwell 1929
diorite	Reid J. H. 1917
diorite, altered	Junner 1920
diorite, propylitized	Junner 1920
dolerite, altered	Nye, Finucane and Blake 1934
feldspar-hornblende	Edwards 1932b
hornblende	Reid J. H. 1917; Simpson 1914a
hornblende, metasomatized	Simpson 1914a
hornblende-quartz	Brown 1928
hypersthene-quartz	Summers 1914b
labradorite	Edwards and Easton 1937a
metamorphosed	Joplin 1935
quartz	Teale 1920
quartz-feldspar	Edwards and Easton 1937a
soda	Farquharson 1914b
Porphyry	Edwards and Easton 1937a; Sherrard 1952; Simpson 1916
adamellite	Kleeman 1937
albite	Farquharson 1916; Stillwell 1929
augite	Mahony 1925b
feldspar	Jack 1917

Porphyry (*continued*)	
feldspar, sericitized	Mahony 1925b
garnetiferous	Stevens 1952
granite	Broadhurst and Campbell 1933; Brown 1928; Joplin 1944
granodiorite	Stevens 1952
hauyne-sanidine-garnet	Edwards 1947
monzonite	Browne and Greig 1922b
quartz	Edwards and Easton 1937a; Farquharson 1914b; Jutson 1921a; New South Wales G. S. 1919; 1927; Reid J. H. 1917; Sherrard 1952; Teale 1920
quartz, altered	Reid A. M. 1923
quartz, topazized	Reid A. M. 1923
quartz-feldspar	Richards 1925a
syenite	Edwards 1947; Nye 1923
Propylite, carbonated	Simpson 1916
Psammite, quartz	Vallance 1953a
tuffaceous	Joplin 1942
Psammopelite	Vallance 1953a
Pyroxene-chlorite-spinel rock	Joplin 1936
Pyroxenite	Brown 1930
altered	Reid A. M. 1923
Quartz-kyanite rock	Talbot 1920
Quartz-plagioclase-epidote-chlorite rock	McWhae 1948
Quartzite	Browne 1922a; Bowley 1923; Chemical Staff 1922; Stillwell 1922
Rhyodacite, biotite	Thomas 1947
Rhyolite	Brown 1931; Ekwards and Easton 1937a; Hills 1929; Joplin 1943; Junner 1915; New South Wales G. S. 1924; Richards 1923b; Richards and Byran 1924; Sherrard 1952; Sussmilch 1922; Sussmilch and Greig 1929; Thomas 1947
soda	Edwards 1932b
Rhyolite tuff	Richards and Bryan 1924
Riebeckite rock	Finucane 1939
Sandstone (altered)	New South Wales G. S. 1920
Sandstone, garnet	Chemical Staff 1922; New South Wales G. S. 1923; Stillwell 1922
Sandstone xenolith	Edwards 1937b
Schist	Farquharson 1916; Joplin 1942; 1945; Tattam 1929; Vallance 1953a
andalusite	Joplin 1942
andalusite-quartz	Clarke 1925
antigorite-tremolite-talc	Basnett 1942
calc-	Simpson 1916
chlorite	Clarke 1914; Simpson 1916; 1930
chlorite-quartz	Farquharson 1917; Feldtmann 1921
chloritoid mica	Simpson 1937
cummingtonite	Simpson 1931
garnet-sillimanite-cordierite	Chemical Staff 1922; Stillwell 1922
graphite	Clarke 1914; Feldtmann 1916
hornblende	Simpson 1916
magnesite	Simpson 1916
mica	Joplin 1942

Schist (*continued*)	
pennine-ferroantigorite-tremolite	Basnett 1942
quartz-chlorite-mica	Joplin 1942
quartz-feldspar-sericite	Browne 1922a
quartz-muscovite	Miles 1943
quartz-sericite	Maitland 1925
sericite	Aldermann 1938; Browne 1922a; Chemical Staff 1922; Joplin 1947;
sericite (xenolith)	Prider 1943
staurolite	Simpson 1921; 1933
talc-chlorite	Simpson 1916
xenolith	Tattam 1929
Serpentine	Bowley 1945; Jutson 1914; 1921b; Prider 1944; Simpson 1916; Vallance 1953a
Shonkinite	Brown 1930
Silicified rock	Simpson 1916
Sillimanite-cordierite-spinel xenolith	Joplin 1947
Sinter (fused)	Baker 1953
Slate	Andrews 1915; Jack 1923; Joplin 1942; 1945; 1947; Mahony 1925a; Mawson and Segnit 1949; New South Wales G. S. 1921; 1925; Prider 1943; Ridgway 1952; Simpson 1916; Stevens 1952; Stillwell 1919; 1929; Tattam 1929; Watson 1925; Winton 1920
chiastolite	Joplin 1942; 1945
chlorite	Farquharson 1916
Spilite	Benson 1915b; Richards and Bryan 1925b; Scott 1951; 1952
Syenite	England 1935; New South Wales G. S. 1924; 1931; 1935; Nye 1923
albite	Segnit 1949
albite-mica	Browne 1920b
ilmenitic	England 1935
quartz	Cochrane and Samson 1950
soda	Broadhurst and Campbell 1933
Syenite-pegmatite	Edwards 1947
Syenite porphyry	Edwards 1947; Nye 1923
Tachylite	Dunn 1914b; Simpson 1916
Teschenite	Edwards 1953c
Tholeiite	Edwards 1936; 1938
Tinguaite	Edwards 1947
sanidine	Edwards 1947
Tonalite	Alderman 1927; Joplin 1931
Toscanite	Morris 1914; Sussmilch and Greig 1929; Thomas 1947
Tourmaline rock	Farquharson 1914b
Trachyandesite	
hornblende	Colditz 1948
hypersthene	Edwards and Crawford 1940
Trachybasalt	
altered	Browne and White 1929
olivine	Mawson 1950
Trachyphonolite	Mahony 1931
Trachyte	Mahony 1931
Trachytic rock	New South Wales G. S. 1925

Tremolite rock	Basnett 1942
Troctolite	Osborne 1920
Tuff	New South Wales G. S. 1918; Scott 1951; Simpson 1916; Teale 1920
rhyolite	Richards and Bryan 1924
zeolitic andesite	Edwards and Glaessner 1953b
Tuff (tuffaceous greywacke)	Edwards and Glaessner 1953b
Tuff (tuffaceous psammite)	Joplin 1942
Ultrabasic zenolith	Vallance 1953a
Variolite	Benson 1915a
Xenolith	
amphibolite	Vallance 1953b
andalusite-cordierite-spinel plagioclase	Osborne 1949
basic	Brown 1928
biotite-hornblende	Osborne 1949
biotite-hornfels	Thomson 1943
cordierite-sillimanite-spinel	Stevens 1952
epidote-biotite	Prider 1945
hornblende-epidote-biotite hornfels	Prider 1943
hornfels	Kleeman 1937
hypersthene-plagioclase-biotite-quartz	Stevens 1952
micaceous	Tattam 1929
olivine-pyroxene	Mahony 1925b
sandstone	Edwards 1937b
schist	Tattam 1929
sericite schist	Prider 1943
sillimanite-cordierite-spinel	Joplin 1947
ultrabasic	Vallance 1953a

List of Published Parts of the Series

Marjorie Hooker (1956) Data of rock analyses, Part I. African periodical and serial literature. *Geochim. et Cosmochim. Acta* **9,** Nos. 1–2, 90–97.

Marjorie Hooker (1956) Data of rock analyses, Part II. Bibliography and index of rock analyses in the African periodical and serial literature. *Geochim. et Cosmochim. Acta* **9,** No. 4, 190–213; Suppl., **11,** Nos. 1–2, 138.

Marjorie Hooker (1957) Data of rock analyses, Part III. New Zealand periodical and serial literature. Bibliography and index of rock analyses. *Geochim. et Cosmochim. Acta* **11,** Nos. 1–2, 130–138.

Marjorie Hooker (1958) Data of rock analyses, Part IV. Icelandic periodical and serial literature. Bibliography of rock analyses. *Geochim. et Cosmochim. Acta* **15,** Nos. 1–2, 30–31.

Geochimica et Cosmochimica Acta, 1959, Vol. 15, pp. 370 to 372. Pergamon Press Ltd. Printed in Northern Ireland

GEOCHEMICAL NOTE

The significance of K/Rb ratios for theories of tektite origin

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EHMANN and KOHMAN (1958) report the presence of the unstable nuclides Al^{26} and Be^{10} in tektites in amounts comparable to the levels in stone meteorites, and much greater than could be produced on the earth. It is concluded that the tektites have been exposed to cosmic radiation outside the earth's atmosphere for at least 10^6 years.

Since UREY (1955) has shown that a cluster of small objects of tektite size would be unstable against the gravitational field of the sun, KOHMAN (1958) has proposed that the tektites come from beyond the solar system. If this is correct the significance of tektites can hardly be overestimated. He suggests that the hypothesis may be tested in two ways:

(1) If they travelled as a loose cluster of objects, the inner particles might be shielded to some extent from the cosmic radiation and, hence, variations should exist in the amount of radioactive nuclides. These variations could be detected by an adequate sampling programme.

(2) If they have come from outside the solar system their isotopic abundance ratios might be expected to differ from the terrestrial abundance pattern, on the basis of current theories of element formation (CAMERON, in press; BURBIDGE *et al.* 1957).

In addition to possible variations in isotopic abundances, differences in elemental abundances might also be expected, particularly in view of the number of element-forming processes operative. A sensitive index of abundance variation should be found in the ratios between closely associated elements, e.g. Zr–Hf, Nb–Ta, the rare earths and K–Rb. However, only sufficient data are available to demonstrate the K–Rb coherence in tektites, chondrites and the earth.

AHRENS *et al.* (1952) first demonstrated the constancy of the K/Rb ratio in terrestrial rocks and chondritic meteorites and this has been considered evidence for a common origin (AHRENS, 1954). This ratio is 220 $\pm$ 50 for chondritic meteorites (HERZOG and PINSON, 1956). PINSON *et al.* (1956), PINSON *et al.* (1957) and PINSON *et al.* (in press) have given K and Rb data for tektites and the K/Rb ratio ranges from 170 to 210, averaging 190. The data are plotted in Fig. 1 which is a modification of Fig. 1 of TAYLOR and HEIER (1958). It is evident that tektites, chondritic meteorites and most terrestrial material have similar K/Rb ratios.

The K/Rb coherence may be altered by extreme geological processes resulting, usually, in Rb enrichment, e.g. in pegmatite feldspars (Fig. 1, I), late stage granites (Fig. 1, II) and lepidolites (Fig. 1, IV), but occasionally in relative Rb impoverishment (Fig. 1, III) (TAYLOR and HEIER, 1958). Apparently no fractionation of K and Rb occurred during the processes of planet and/or meteorite formation, although this fractionation has occurred on a minor scale in the earth's crust during geological time.

The similarity of K/Rb ratios for the earth, chondrites and tektites is supporting evidence for an origin of the tektites within the solar system. Alternatively, if they formed from another stellar dust cloud, then this system had the same relative proportions of K and Rb as the solar system.

It is of interest to examine this possibility. One of the most significant results of recent astrophysical research has been the recognition of the fact that the universe, or even our galaxy, is not of uniform chemical composition. It also appears likely that elements heavier than hydrogen have been synthesized in stellar interiors and that some of this material is returned to the interstellar medium and incorporated in later formed stars (and associated planetary systems). The composition of stars is thus dependent on time and place of origin (CAMERON, in press).

Burbidge *et al.* (1957) in an extensive survey list the various processes of nuclear synthesis in stars. The three potassium isotopes are formed almost exclusively by neutron capture reactions on a long time scale; the so-called slow or *s*-process which is thought to occur in the interiors of red giants and which operates on a time scale of 100 to 10^5 years. Some Rb^{85} is formed by this process. However, it is also formed by neutron capture on a fast time scale; the so-called rapid or *r*-process, operating in times of the order of from 0·1 to 10 sec. This is thought to take place in supernovae. Rb^{87} is formed exclusively by the *r*-process. From consideration of the time involved to condense the solar system (10^7–10^8 years), the rate of supernovae explosions (3×10^6 in 10^9 years) and the rate of dispersion of elements from supernovae, Burbidge *et al.* (1957, p. 639) conclude that, "it does not appear unreasonable . . .

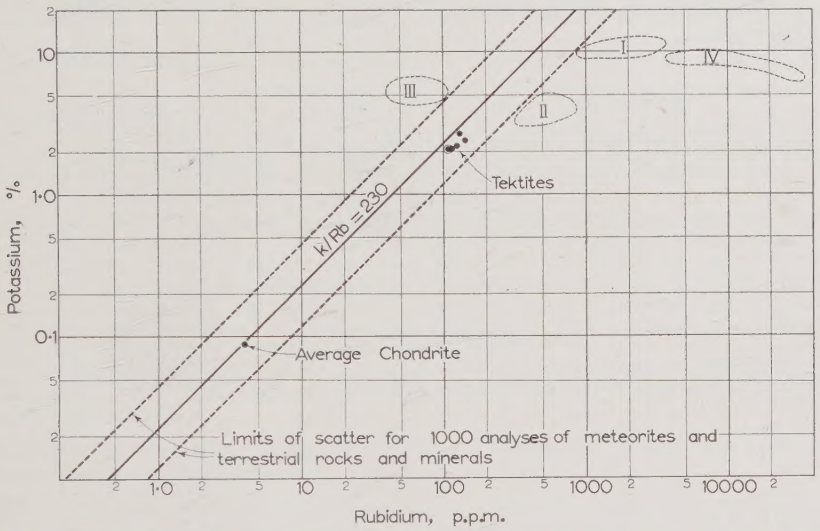

Fig. 1. Potassium–rubidium relationship for rocks, minerals, meteorites and tektites, showing close association of the two elements. Areas of abnormal K/Rb ratios in terrestrial materials are shown by I (sixteen analyses of pegmatite feldspars); II (seven analyses of late-stage granites); III (nine analyses of feldspars depleted in Rb) and IV (twenty-two analyses of lepidolites).

that a single supernova has been responsible for all the material built by the *r*-process currently present in the solar system."

Thus, if all the Rb^{87} and some of the Rb^{85} in the solar system is due to such an event, while the abundance of potassium isotopes is controlled by the *s*-process operative in a different environment on a different time scale, it becomes apparent that the K/Rb elemental ratio is not constant throughout the universe and that the solar system ratio of about 220 is possibly unique.

The ratio K/Rb is evidently sensitively dependent on conditions of element formation; since, therefore, the ratio in the tektites is the same as that in the earth and chondrites, either the tektites have originated from within the solar system or they have come from some other cosmic material which has had an identical history: this seems a remote possibility.

These considerations strengthen the case for an origin of tektites with the solar system.

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References

Ahrens L. H. (1954) Distribution of minor elements in rocks. *Nature, Lond.* **174,** 811–816.

Ahrens L. H., Pinson W. H. and Kearns M. M. (1952) Association of rubidium and potassium and their abundances in common igneous rocks and meteorites. *Geochim. et Cosmochim. Acta* **2,** 229–242.

Burbidge E. M., Burbidge G. R., Fowler W. A. and Hoyle F. (1957) Synthesis of the elements in stars. *Rev. Mod. Phys.* **29** (4) 547–650.

Cameron A. G. W. (1959) The origin of the elements. *Phys. Chem. Earth* **3**. In press.

Ehmann D. and Kohman T. P. (1958) Cosmic-ray-induced radioactivities in meteorites—II. Al^{26}, Be^{10} and Co^{60}, aerolites, siderites and tektites. *Geochim. et Cosmochim. Acta* **14,** 364–369.

Herzog L. F. and Pinson W. H. (1956) Rb/Sr age, elemental and isotopic abundance studies of stony meteorites. *Amer. J. Sci.* **254,** 555–566.

Kohman T. P. (1958) Are tektites extra-solar-system meteorites? *Nature, Lond.* **182,** 252–253.

Pinson W. H., Fairbairn H. W., Herzog L. F. and Cormier R. F. (1957) Sr/Rb age study of tektites. *Bull. Geol. Soc. Amer.* **68,** 1780.

Pinson W. H., Herzog L. F. and Cormier R. F. (1956) Age study of a tektite. *Bull. Geol. Soc. Amer.* **67,** 1725.

Pinson W. H., Herzog L. F., Fairbairn H. W. and Cormier R. F. (1958) Sr/Rb *Age Study of Tektites*. Annual Progress Report NYO 3938 USAEC, 82–96.

Pinson W. H., Herzog L. F., Fairbairn H. W. and Cormier R. F. (1958) Sr/Rb age study of tektites. *Geochim. et Cosmochim. Acta* **14,** 331–339.

Taylor S. R. and Heier K. S. (1958) Rubidium depletion in feldspars. *Nature, Lond.* **182,** 202–203.

Urey H. C. (1955) On the origin of tektites. *Proc. U.S. Nat. Acad. Sci. Wash.* **41,** 27.

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